

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

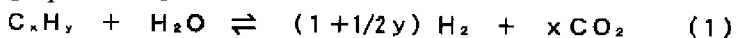
[Field of the Invention] This invention relates to the film which penetrates hydrogen selectively from a steam or ethylene glycol. This transmission film is used suitably for the separation or the penetration of gas under the conditions in which the polar high compound steam of water, ethylene glycol, gamma-butyrolactone, ammonia, etc. exists. This transmission film can be used also as the film for various gas permeation under the situation where a polar high compound steam does not exist, of course, or a film for a liquid penetration.

[0002] This invention relates to application and the pertinent art of this transmission film again. The transmission film of this invention can be used for the use of a fuel cell, an electrolytic condenser, etc., for example.

[0003] Although a fuel cell uses hydrogen as fuel, this hydrogen is obtained by receiving supply of direct hydrogen or reforming hydrocarbon, such as methanol, methane, and gasoline, with a steam etc. The system which supplies hydrogen directly is advantageous at the point which can simplify the structure of a system. However, when a high-pressure-hydrogen cylinder and a liquid hydrogen tank are used, it is a problem in respect of safety or weight, and when a hydrogen storing metal alloy is used, the point of a price and weight poses a problem. It is a problem also at the point that the infrastructure for supplying hydrogen is not fixed. On the other hand, although a reformer etc. are needed and the structure of a system is complicated, the method of reforming hydrocarbon has a lightweight fuel stores dept., and it is thought that maintenance of the infrastructure which supplies fuel is easier for it than hydrogen. When a steam is used for refining of hydrocarbon, the following reactions occur with a reformer.

[0004]

[Equation 1]



[0005] Since this reaction is static reaction, if hydrogen and carbon dioxide are selectively removable from a reformer, it can advance a reaction more. Therefore, the film which penetrates selectively hydrogen which is a resultant from the water which is reaction raw materials is very important.

[0006] A small amount of carbon monoxide mixes in reformed gas by the water gas shift reaction shown below.

[0007]

[Equation 2]



[0008] It is known that carbon monoxide will carry out poisoning of the catalyst on a fuel electrode. Therefore, generation of CO can be suppressed if H₂ and CO₂ are quickly removable from a reforming reaction system. The film which penetrates hydrogen

selectively can also remove the carbon monoxide which is a poisoning substance of a fuel electrode, and is still more useful than carbon monoxide. If it is not a film which penetrates hydrogen selectively from water also in this case, the water which lives together in reformed gas will adsorb in membranous fine pores, and the transmission quantity of hydrogen will decrease. Therefore, the film which penetrates hydrogen selectively is very more important also in separation of the hydrogen/carbon monoxide gas under existence of a steam than in water.

[0009]The transmission film of this invention can also be used for an electrolytic condenser. The electrolysis solution is held in a hermetic container, an electrolysis solution decomposes gradually during an electrolytic condenser operation, and hydrogen gas generates an electrolytic condenser. The electrolytic condenser had caused breakage with the pressure of the emitted hydrogen gas. If the transmission film of this invention is used, the life of an electrolytic condenser can fully be extended and the safety of an electrolytic condenser in use can also secure it.

[0010]

[Description of the Prior Art]Conventionally, palladium membrane is known as a film which makes hydrogen penetrate selectively. For example, in steam reforming of methane, it is also possible to lean a reaction equilibrium to the output side remarkably by making the hydrogen to generate penetrate selectively. However, the hydrogen permeation mechanism of palladium membrane is a dissolution diffusion mechanism accompanied by dissociation of hydrogen.

In order for a utilization level to gather a transmission rate, hydrogen gas must be supplied by not less than 300 ** and tens of atmospheres.

The application for the fuel cell and electrolytic condenser use of this penetration condition from severity is difficult. Palladium is dramatically expensive and it is difficult to use in practice industrially also from this point.

[0011]As a method of removing carbon monoxide from the gas (example: gas which carried out steam reforming of the hydrocarbon) containing the hydrogen supplied to a fuel cell, the method of oxidizing only carbon monoxide selectively on a catalyst is proposed. In JP,11-130406,A, the method of making oxygen react to reformed gas on the catalyst which supported platinum group system metal to zeolite, and removing carbon monoxide is proposed. In JP,10-247154,A, the method of using the catalyst which supported rhodium and a ruthenium to zeolite, silica, or alumina is proposed. However, in these methods, since a selective oxidation catalyst tower and its heating unit are carried, a device is large and is complicated. When a steam superfluous at the time of refining is used, into reformed gas, a steam mixes, catalytic activity is reduced, and a superfluous steam cannot be removed.

[0012]On the electrolytic condenser field and in JP,62-112314,A or JP,62-272515,A, Although the method of discharging the hydrogen gas emitted in an electrolytic condenser outside using the transmission film of the shape of a hollow filament which consists of polyimide, poly ethylene tetrafluoride, or polypropylene, etc. are proposed, an effect until it still discharges hydrogen gas enough and carries out internal pressure rise prevention is not enough. In an electrolytic condenser, since an electrolysis solution penetrated as a steam from an electrolytic condenser, there was a big fault that the presentation of internal electrolysis liquid changed and the characteristic of an electrolytic condenser changed.

[0013]Although the film using zeolite is studied briskly in recent years, it is difficult to obtain zeolite membrane with the specific penetration characteristic with sufficient reproducibility. Although hydrogen permeation speed in 25 ** penetrates well the film which are $10 \times 10^{-7} \text{ mol / (m}^2\text{/s/Pa)}$ above, and (1) (2) hydrogen, a steam and/or ethylene glycol are not proposed until now about the zeolite membrane which is hard to penetrate.
[0014]

[Problem(s) to be Solved by the Invention]The purpose of this invention is what is going to cancel the fault of the above-mentioned conventional technology, It is in providing the film which cannot penetrate easily (2) ethylene-glycol steam which is excellent in heat resistance and chemical resistance, penetrates hydrogen well excluding expensive metal substantially like hydrogen and affinitive palladium, and cannot penetrate a steam as easily as (1) hydrogen.

[0015]Other purposes of this invention are related with application and the pertinent art of this transmission film, and there are in providing the fuel cell system which has the above-mentioned transmission film which utilizes the permeability of the above-mentioned transmission film effectively, the steam-reforming device of hydrocarbon, and an aluminium electrolytic condenser.

[0016]

[Means for Solving the Problem]To achieve the above objects, as a result of inquiring wholeheartedly, it resulted in an invention which has the following composition.

[0017]The invention of this invention according to claim 1 is hydrogen permeation speed in 65 **. V_{H_2} ($\text{mol}/(\text{m}^2 \text{ and s-Pa})$) and water vapor transmission rate Ratio of V_{H_2O} ($\text{mol}/(\text{m}^2 \text{ and s-Pa})$) V_{H_2}/V_{H_2O} 20 or more. And hydrogen permeation speed in 85 **. V_{H_2} ($\text{mol}/(\text{m}^2 \text{ and s-Pa})$) and ethylene glycol steamy transmission rate Ratio with V_{EG} ($\text{mol}/(\text{m}^2 \text{ and s-Pa})$) That V_{H_2}/V_{EG} is 50 or more. It is a transmission film which does not use as the main ingredients palladium by which it is characterized.

[0018]The invention of this invention according to claim 2 is a transmission film which fills the following (1) and the characteristic of (2).

[0019](1) Hydrogen permeation speed in 25 ** should be more than $10 \times 10^{-7} (\text{mol}/(\text{m}^2 \text{ and s-Pa}))$.

[0020](2) When you stop a test tube containing ethylene glycol by this film, you put into 85 ** oven and you measure the loss-in-quantity speed, the value should be below $6 \times 10^{-3} (\text{g}/\text{hour})$ per 1 cm of film ².

[0021]A process of zeolite membrane which processes with a steam a filmy material which has that boehmite or quasi-boehmite is used for this invention as an alumina source and/or a silica source, and an alumina source is included.

[0022]An electrolytic condenser which has a transmission film or zeolite membrane of a steam-reforming device and the above-mentioned statement which has a transmission film or zeolite membrane of a fuel cell system and the above-mentioned statement in which this invention has a transmission film or zeolite membrane of the above-mentioned statement is contained.

[0023]A method of making a transmission film or zeolite membrane of the above-mentioned statement of reformed gas contact, and making hydrogen penetrate from reformed gas more nearly selectively than a steam, after this invention reforms hydrocarbon with a steam is contained.

[0024]The invention of this invention according to claim 14 is an invention about a

separation method of a gas which used a transmission film or zeolite membrane of a statement for the above, or a fluid.

[0025]

[Embodiment of the Invention] This invention is explained in full detail below.

[0026] First, the transmission film of this invention is explained.

[0027] The transmission film of this invention is hydrogen permeation speed in 65 **, V_{H_2} (mol/(m² and s-Pa)) and water vapor transmission rate Ratio of V_{H_2O} (mol/(m² and s-Pa)) V_{H_2}/V_{H_2O} 20 or more. And hydrogen permeation speed in 85 **, V_{H_2} (mol/(m² and s-Pa)) and ethylene glycol steamy transmission rate Ratio with V_{EG} (mol/(m² and s-Pa)) That V_{H_2}/V_{EG} is 50 or more. It is a transmission film which does not use as the main ingredients the palladium by which it is characterized. As a film which hydrogen penetrates selectively, although precise films, such as palladium membrane, are known, what penetrates hydrogen with selectivity higher than a steam and ethylene glycol by the film which does not use palladium as the main ingredients is not known until now.

[0028] This invention relates to the transmission film which fills the following (1) and the characteristic of (2).

[0029] (1) The hydrogen permeation speed in 25 ** should be more than 10×10^{-7} (mol/(m² and s-Pa)).

[0030] (2) When you stop the test tube containing ethylene glycol by this film, you put into 85 ** oven and you measure the loss-in-quantity speed, the value should be below 6×10^{-3} (g/hour) per 1 cm of film².

[0031] While a room temperature shows a big hydrogen permeation speed in this way, the film which cannot penetrate ethylene glycol easily is not known until now.

[0032] Although the whole transmission film of the transmission film said here may be made of construction material which has hydrogen permeation selectivity, in order that it may usually enlarge a transmission rate, The method of supporting the film which penetrates hydrogen selectively is liked and used from a steam and/or ethylene glycol on the porous support which has macro pore. Thus, the film which penetrates hydrogen selectively from the steam and/or ethylene glycol which were supported on macro pore porous support is called stratum functionale (or functional membrane). In order to show the permeability of the invention film indicated to claim 2, the thinner one of the thickness of the stratum functionale is preferred. Although the desirable thickness of the stratum functionale changes with raw materials of the stratum functionale to choose, 500 micrometers or less are 100 micrometers or less desirable still more preferably. If the stratum functionale is thin, the thinner one is preferred, but it becomes not much thin too much, and compactness must not be lost. It is saying that there being compactness does not have a hole resulting from the pinhole or defect instead of a meaning of being nonporous.

[0033] It is used in order to prevent the portion of the stratum functionale weak [intensity] or weak from the porous support used by this invention breaking thinly, and the upright thing of porous support is preferred.

[0034] It may be unable to simplify and, in the case of porous support which becomes, the stratum functionale may be unable to be protected from destruction. In the film of intensity which the porous support itself touches by hand simply, and breaks, it is not suitable for industrial practical use.

[0035] Since this invention relates to a transmission film, as a base material which

supports the stratum functionale, the porosity of the grade which does not check the permeability of the stratum functionale is required for it.

[0036]If the construction material of porous support has the above character, it will not be limited in particular, but ceramics, such as metal and a metallic oxide, and organic polymer are mentioned as an example. From a viewpoint of intensity or stiffness, ceramics, such as metal and a metallic oxide, are used preferably. From a viewpoint heat-resistant and chemical-resistant, a metallic oxide is used most preferably especially. Especially as a metallic oxide, although not limited, alumina, zirconia, silica, mullite, cordierite, a titania, zeolite, or a zeolite prototype is used preferably. As a metaled example, the porous support made from stainless steel (sintered metal), etc. are mentioned. In the use for which heat resistance is not required, if the porous support of organic polymer is also upright, it can use. In order to prevent destruction of a stratum-functionale portion also in this case, when it is going to bend by hand, what has the stiffness of the grade at which it does not see and turn by the eye is preferred.

[0037]The thing of shape usually marketed, such as a globular shape, plate-like, tube shape, the shape of a monolith, and honeycomb shape, can be used, for example, without also limiting especially the shape of porous support. When using for an electrolytic condenser, porous support is the shape where a cylindrical plate is the most preferred.

When using it as a demarcation membrane, high surface area is required for porous support, and it is preferred that it is the shape of a tube, a monolith, or honeycomb shape.

[0038]The manufacturing method of porous support used by this invention, Although not limited in particular, usually the auxiliary agent and binder for molding can be added to powder, such as remaining as it is or ceramics, and extrusion molding of the powder, such as ceramics, can be carried out to it, or press forming can be performed, and the method of manufacturing can be adopted through processes, such as desiccation and calcination.

[0039]Although the optimal calcination temperature changes with raw materials of porous support, its temperature which is a grade from which sintering begins for a while is desirable in respect of intensity. Although suitable calcination temperature changes with sizes of a raw material or particles, generally it is 900-1,400 °C especially preferably 800-1,500 °C preferably 600 °C - 2,000 °C. Washing by a drug solution etc., etc. may be processed after calcination. Coating with fine particles, controlling the pore diameter of porous support by methods, such as dip coating, controlling compatibility with the stratum functionale by them, or controlling surface roughness by them is also preferably performed to the fabricated porous support. Although the layer by such coating etc. is called interlayer, providing one or more layers of this interlayer is preferably performed, also when using which stratum functionale.

[0040]When the pore diameter of porous support is too large, the stratum functionale does not film-ize, but a hole produces, or, Or it is got blocked, and since the distance in which stratum-functionale raw material liquid permeates too much into the fine pores of porous support, and the hole of porous support is eventually closed by the stratum functionale and in which gas penetrates the inside of the stratum functionale becomes long too much, the fault that sufficient amount of gas permeation is not obtained may arise. Therefore, 10 micrometers or less are preferred and 5 micrometers or less of average pore sizes [1 micrometer or less of] of porous support are less than 0.5 micrometer especially preferably still more preferably still more preferably. Thus, the

above-mentioned interlayer is preferably used also in the meaning which controls a pore diameter. Although the minimums of an average pore size differ and cannot be specified with the molecular size made to penetrate, it is better for there to be an average pore size of 0.01 micrometers or more from a penetrable viewpoint of a request molecule.

[0041]The average pore size of porous support can usually be measured using the mercury porosimeter. If the size of the ceramics particles which constitute the interlayer is uniform in simple, even if the size of the particle is called average pore size, there will be no great difference.

[0042]The stratum functionale may be formed in any portion of porous support in the transmission film of this invention. The stratum functionale can be formed in both one side of porous support, both the surfaces, or the surfaces and insides. When forming the stratum functionale, in the point of control of the thickness of the stratum functionale, it is preferred to coat on the surface of porous support, and it is preferred to form in the inside of porous support in respect of the intensity of the stratum functionale. In tube shape porous support, even if it coats the inside, it does not matter even if it coats outside. Also in the porous support of the shape of a monolith, or honeycomb shape, although the stratum functionale may be provided anywhere, since surface area can do greatly the direction coated inside in these cases, it is desirable.

[0043]The measuring method of the hydrogen permeation speed said by this invention is described below. For example, 2-atmosphere hydrogen gas is supplied to one side of the transmission film of 1 cm^2 , and the gas volume penetrated from a membranous opposite hand is measured with a soap film flow meter. If this method is used, a transmission rate when 1 cc/s of hydrogen gas penetrates will serve as $4.5 \times 10^{-6}\text{ (mol/(m}^2\text{ and s-Pa))}$.

[0044]The range of the hydrogen permeation speed measured with the described method is described. Even if too large [the hydrogen permeation speed of a transmission film is too small, and], a problem produces it. When hydrogen permeation speed was smaller than $1 \times 10^{-7}\text{ (mol/(m}^2\text{ and s-Pa))}$, for example it applies to the fuel cell mentioned later, in order to make the amount of hydrogen gas generated from a reformer penetrate, a huge membrane area is needed, and it is not suitable for utilization. Therefore, the transmission rate of hydrogen needs to be more than $1 \times 10^{-7}\text{ (mol/(m}^2\text{ and s-Pa))}$, and more than its $10 \times 10^{-7}\text{ (mol/(m}^2\text{ and s-Pa))}$ is more preferred. If hydrogen permeation speed is smaller than $1 \times 10^{-10}\text{ (mol/(m}^2\text{ and s-Pa))}$ when it applies to the electrolytic condenser mentioned later for example, The amount of hydrogen gas generated inside an electrolytic condenser will increase more than the quantity emitted to the electrolytic condenser exterior through a transmission film, as a result, the hydrogen pressure inside an electrolytic condenser will increase, and an electrolytic condenser will be destroyed. Therefore, the transmission rate of hydrogen needs to be more than $1 \times 10^{-10}\text{ (mol/(m}^2\text{ and s-Pa))}$, and more than its $1 \times 10^{-9}\text{ (mol/(m}^2\text{ and s-Pa))}$ is more preferred.

[0045]Although the maximum in particular of a transmission rate is not limited, it is preferred. [of the one smaller than $1 \times 10^{-5}\text{ (mol/(m}^2\text{ and s-Pa))}$] This is because not only hydrogen but other ingredients are penetrated well, so selectivity may be lost as a result when a transmission rate is larger than $1 \times 10^{-5}\text{ (mol/(m}^2\text{ and s-Pa))}$.

[0046]As for the transmission film of this invention, it is desirable for hydrogen permeation speed to be not only beyond constant value, but for the ratio of hydrogen permeation speed to a water vapor transmission rate to be beyond constant value. The measuring method of the water vapor transmission rate is as follows. This transmission

film stops the test tube containing water, it puts into a 65 °C dryer, and the loss-in-quantity speed is measured. If the steam pressure of the water in 65 °C assumes the steam concentration in 2.5×10^{-4} Pa and a dryer to be 0 Pa, a water-vapor-pressure power difference will serve as 2.5×10^{-4} Pa. A water vapor transmission rate is drawn from transmission time, a membrane area, and weight loss in quantity, and a unit is made into $(\text{mol}/(\text{m}^2 \text{ and s-Pa}))$. this value -- water vapor transmission rate: -- it is considered as $V_{\text{H}_2\text{O}}$ $(\text{mol}/(\text{m}^2 \text{ and s-Pa}))$. this invention film -- the ratio of the value and hydrogen permeation speed: V_{H_2} $(\text{mol}/(\text{m}^2 \text{ and s-Pa}))$ in 65 °C -- it is preferred that $V_{\text{H}_2}/V_{\text{H}_2\text{O}}$ is 20 or more. This value is so preferred that it is large, and 30 or more are still more preferred.

[0047]And as for the transmission film of this invention, it is desirable for the ratio of hydrogen permeation speed to an ethylene glycol transmission rate to be beyond constant value. The measuring method of the ethylene glycol transmission rate is as follows. This transmission film stops the test tube containing ethylene glycol, it puts into 85 °C oven, and the loss-in-quantity speed is measured. If the steam pressure of ethylene glycol in 85 °C assumes the ethylene glycol concentration in 1.05×10^{-3} Pa and a dryer to be 0 Pa, an ethylene glycol pressure differential will serve as 1.05×10^{-3} Pa. An ethylene glycol transmission rate is drawn from transmission time, a membrane area, and weight loss in quantity, and a unit is made into $(\text{mol}/(\text{m}^2 \text{ and s-Pa}))$. this value -- ethylene glycol transmission rate: -- it is considered as V_{EG} $(\text{mol}/(\text{m}^2 \text{ and s-Pa}))$. this invention film -- the ratio of the value and hydrogen permeation speed: V_{H_2} $(\text{mol}/(\text{m}^2 \text{ and s-Pa}))$ in 85 °C -- it is preferred that $V_{\text{H}_2}/V_{\text{EG}}$ is 50 or more. This value is so preferred that it is large, and 100 or more are still more preferred.

[0048]If the notation unit of loss in quantity of ethylene glycol is set to $\text{g}/\text{cm}^2 \text{ and h}$, it is loss-in-quantity speed in 85 °C. It is preferred that it is below $6 \times 10^{-3} \text{g}/\text{cm}^2 \text{ and h}$. This value is so preferred that it is small, and it is still more preferred that it is below $5.5 \times 10^{-3} \text{g}/\text{cm}^2 \text{ and h}$.

[0049]The hydrogen permeation speed although the heat resistance in particular of the transmission film in this invention is not limited, after performing once heat-treatment in the air of (1) to (3) shown below in order of (1) to (3), It is preferred that the hydrogen permeation speed after carrying out twice in order of (1) to (3) has the heat resistance which does not change not less than 10%.

[0050](1) It is a part for 0.6 °C/from a room temperature to 550 °C, and is temperature up.

[0051](2) Hold at 550 °C for 4 hours.

[0052](3) Lower the temperature by a part for 1.2 °C/from 550 °C to a room temperature.

[0053]The ingredient for which it adheres to a membrane surface or an inside and the transmission rate is reduced by performing the above-mentioned processing once is removable. The hydrogen permeation speed after processing needs to be a value which shows transmission quantity sufficient when it is used for the use which makes hydrogen penetrate, It is preferred that it is more than $1 \times 10^{-10} (\text{mol}/(\text{m}^2 \text{ and s-Pa}))$, and more than $1 \times 10^{-9} (\text{mol}/(\text{m}^2 \text{ and s-Pa}))$ is more preferred. The hydrogen permeation speed after performing heat-treatment in the air of (1) to (3) once in order of (1) to (3), I hear that that the hydrogen permeation speed after carrying out twice in order of (1) to (3) does not change not less than 10% has the heat resistance which is a grade from which permeation performance does not change with above-mentioned heat treatments, and the film of this invention has it. It is required to be a value which shows transmission quantity sufficient when the hydrogen permeation speed after 2 times processing is also used for the use

which makes hydrogen penetrate, It is preferred that it is more than 1×10^{-10} (mol/(m² and s-Pa)), and more than 1×10^{-9} (mol/(m² and s-Pa)) is more preferred.

[0054]Although the raw material of the transmission film used for this invention is not limited, it is preferred that at least one ingredient of the following ingredient of (1) to (5) is included.

[0055](1) Zeolite given in the zeolite (2) inorganic-oxide particle (3) silicone rubber, silicone resin, or silicone oil (4) organic-polymer-compound (5) carbon above (1) is a crystalline inorganic oxide with the pole diameter of molecular size. Molecular size is the range of the size of the molecule which exists in a world, and, generally, means the range of about 0.2 to 2 nm. Zeolite is the crystalline micro porous substance which comprised crystalline silicate, crystalline aluminosilicate, crystalline metallosilicate, crystalline alumino phosphate, or crystalline metalaw alumino phosphate.

[0056]Crystalline silicate, crystalline aluminosilicate, crystalline metallosilicate, The kind in particular of crystalline alumino phosphate and crystalline metalaw alumino phosphate does not have restriction, For example, atlas TAIPUSU OBU (Mayer) Zeolite Structure Orson, Valle Rocha, ZEORAITSU, 17 (1/2), 1996 (Atlas of Zeolite Structure types (W. M. Meier, D. H. Olson, Ch. Baerlocher, Zeolites, and 17 (1/2).)) A crystalline inorganic porous substance with the structure published by 1996 is mentioned.

[0057]As a kind of zeolite, the smaller one of the diameter of a fine-pores entrance which the crystal has is preferred, and 0.8 nm or less especially its 0.2 nm or more is preferred. It is 0.6 nm to 0.2 nm preferably. Although expression often called an oxygen n membered-ring in the size of fine pores is used in zeolite, the zeolite of 12 membered-rings is preferably used from a five-membered ring in this invention. It is zeolite of ten or less membered-rings especially preferably. As an example of such zeolite, it is atlas structure TAIPUSU (Mayer). OBU Zeolite Orson, Valle Rocha, ZEORAITSU, 17 (1/2), 1996 (Atlas of Zeolite Structure types (W. M. Meier, D. H. Olson, Ch. Baerlocher, Zeolites, and 17 (1/2).)) The zeolite published by 1996, It is ABW, AEI, AFG, AFT, AFX, ANA, APC, ATN, ATO, ATT, ATV, AWW, BIK, BRE, CAN, CA S, CHA, CHI, DAC, DDR, DOH, EAB, EDI, ERI, EUO, when they are said with the structure expressed with three characters. FER, GIS, GOO, JBW, ZK-5, LAU, LEV, LIO, LOS, LOV, LTA, LTN, MEL, MEP, MER, MFI, MFS, MON, MTN, MTT, N ON, PAU, RHO, RON, RSN, RTE, RTH, RUT, SGT, The zeolite of THO, TON, VET, VNI, VSV, WEI, WEN, YUG, and ZON structure is mentioned. Although zeolite structure in particular is not limited, by this invention, MFI mold structure is fond and it is used.

[0058]Although the presentation of zeolite does not have restriction in particular, what has many silica components is preferred. Generally, zeolite can divide a molecule with a size difference so that it may be called a molecular sieve. Each minimum molecular size (kinetic diameter MTA: Kinetic Diameter) of hydrogen, water, carbon monoxide, and carbon dioxide, They are 0.29, 0.26, 0.38, and 0.33 nm, respectively (zeolite molecular written by Breck sieves (1974 JON wheelie and Suns publication) p636-637), In view of the relation of the minimum molecular size, it is dramatically difficult to make only hydrogen penetrate selectively from the gas of the mixed stock of water and hydrogen. This invention has an important meaning in the meaning which realized the penetration of only such difficult hydrogen. Although the mechanism of the selection penetration of only such hydrogen is not yet clarified, there are fine pores of the size which penetrates

hydrogen and it is thought required for the membranous surface and/or fine pores to have the hydrophobic character which crawls water. As for zeolite, if it carries out from such a viewpoint, it is preferred to use the thing of high silica or pure silica. Therefore, zeolite is crystalline silicate, crystalline aluminosilicate, crystalline metallosilicate zeolite, or a zeolite prototype, and since especially the thing of high silica is considered that the inside of fine pores is hydrophobicity, it is preferred. For example, SiO_2 / aluminum $_2\text{O}_3$ ratio is used as a method of expressing the concentration of the silica components in crystalline aluminosilicate. Zeolite shows hydrophobicity, so that this value is large. Although the range in particular of SiO_2 /aluminum $_2\text{O}_3$ is not limited, by this invention, 30 or more things are fond and it is used.

[0059]Although the abundance of hetero atoms other than silicon and oxygen generally calls high silica the case where the rate of silicon/hetero atom is five or more in a mole ratio, about silica, in this invention, desirable still more preferably, ten or more are 30 or more, and it is 50 or more especially preferably. This number is so preferred that it is large.

[0060]Pure silica is the zeolite which comprised only silica substantially. As a structure which can do such zeolite, Atlas TAIPUSU OBU (Mayer) Zeolite structure Orson, Valle Rocha, ZEORAITSU, 17 (1/2), 1996): Atlas of Zeolite Structure types (W. M. Meier, D. H. Olson, Ch. Baerlocher, Zeolites, and 17 (1/2).) The zeolite published by 1996, Them. When it says with the structure expressed with three characters, ANA,BIK,BRE,CAN,CAS,CHA,CHI,DAC,DDR,DOH,EAB,EDI,ERI,EUO,FER,GIS,JB W,KFI,LAU,LEV,LTA,MEL,MEP,MER,MFI,MFS, motor octane number, MTN, MTT, NON, PAU, RHO, RON, RTE, RTH, RUT, SGT, THO, TON, VET, WEI, and YUG structure are mentioned. As a structure which can make the thing of high silica easily especially, the zeolite of DDR, DOH, EUO, FER, LEV, MEL, MEP, MFI, MFS, MTN, MTT, NON, RTE, RTH, RUT, and TON structure is mentioned. The most desirable structure is MFI structure. This is because it is easy to crystallize and easy to generate a film.

[0061]However, the zeolite of this invention is not restricted to this example. After the above-mentioned reference is published, the newly found-out zeolite, for example, CFI etc., (CIT-5) is contained in the zeolite of this invention. Of course, even if zeolite itself is not a thing of high silica or pure silica, the zeolite which the portion in contact with distributed gas should just have hydrophobicity, for example, performed hydrophobing processing to the surface can be used. Although the method in particular of the hydrophobic treatment is not limited, any method which is generally publicly known can be used. As the example, processing by silane coupling agents, such as silicone compounds, such as silicone rubber, or alkyl alkoxysilane, and alkyl chlorination Silang, processing by the water-repellent grant agent of a fluorine system, etc. are mentioned. Although a processing method in particular is not limited, zeolite membrane is performed, for example in the silicone series coating agent liquid distributed or dissolved in solvents, such as water, immersion or by making contact or applying. The transmission film which is the stratum functionale which consists of zeolite by which the outermost superficial layer was especially covered with the silicone compound is especially used preferably by this invention.

[0062]When the stratum functionale is zeolite, the surface of a zeolite crystal, Since many OH radicals exist, when the fluid of the hydrophilic nature of water, ethylene

glycol, or gamma-butyrolactone contacts the functional membrane surface, liquid membrane is formed in the surface and gas permeation may not happen to it for a while, for example. However, when the outermost surface is thinly processed with the silicone compound, it is an advantage of applying a silicone compound to the outermost surface that become a drop and do not adhere as liquid membrane even if the fluid of the above hydrophilic nature contacts, but the influence on gas permeation nature decreases.

[0063](2) inorganic-oxide particles and (3) silicone rubber which are used as other raw materials by this invention, silicone resin or silicone oil, (4) organic polymer compounds, and (5) carbon are explained in detail later.

[0064]Although the coating method in particular to the porous support of zeolite is not limited, generally, the porous support which provided porous support or an interlayer is directly coated with the film containing zeolite, or the film of organic and/or inorganic polymer is made to contain it, and it is coated. Henceforth, porous support decides to also include the porous support which provided the interlayer.

[0065]Although the manufacturing method in particular of the transmission film containing zeolite is not limited, it can apply the method generally known. For example, when zeolite membrane is coated on a base material on a base material, How to attach a base material in the precursor gel for compounding zeolite, and carry out water heat treatment (example: JP,63-291809,A), How to attach to precursor gel and carry out water heat treatment of it to it beforehand, after carrying out the coat of the seed crystal of zeolite to a base material (example: JP,7-109116,A), Methods (JP,5-50331,B), such as the method (steam method) (example: JP,7-89714,A) of drying, after coating a support surface with precursor gel, and processing with a steam after that, or the method of coating zeolite particles as it is, are applicable. The film made by the method of drying after coating a support surface with precursor gel, and processing with a steam after that is excellent in respect of hydrogen permselectivity, and is used preferably. In order that this method may coat only the precursor of a complement on a base material, there is the strong point with little waste fluid.

[0066]A zeolite precursor is a mixture which carries out fixed time heating and can become zeolite, and a silica source, an alkali source, an organic template, water, etc. are contained. An alumina source etc. are included if needed. Indispensable things are a silica source and water here, and other things change with kinds of zeolite to make.

[0067]As a silica source, colloidal silica, fumed silica, water glass, precipitated silica, a silicon alkoxide, etc. are used. An alkali source is hydroxide of alkaline metals, such as sodium hydroxide, lithium hydroxide, and a potassium hydrate, etc.

[0068]An organic template is a mold agent of an organic compound which builds the hole of zeolite, Quarternary ammonium salt, such as tetraethylammoniumhydroxide, tetrapropylammonium hydroxide, and tetrabutylammonium hydroxide, crown ether, alcohol, etc. are used.

[0069]The alumina source is required when making crystalline aluminosilicate zeolite. For example, aluminum salts, such as boehmite which is hydrated alumina, quasi-boehmite or an aluminium nitrate, aluminum sulfate, and an aluminium chloride, or aluminium hydroxide, an aluminum oxide, aluminum alkoxide, etc. can be used. Boehmite and quasi-boehmite are fond and especially the aluminum source used by this invention is used, although not limited. The boehmite said here is hydroxylation alumina expressed with $\text{AlO}(\text{OH})$. This is obtained by carrying out hot water processing of the

aluminium hydroxide ($\text{aluminum}(\text{OH})_3$) at 150-375 °C. The hydroxylation alumina which has other structures mixes with the steam treatment temperature and steam concentration at the time of this hot water processing. They are called quasi-boehmite. Pural of Condea, etc. are known for the commercial item.

[0070]The method in particular of coating a base material with the seed crystal of zeolite and the precursor of zeolite is not limited, but can apply any publicly known methods. For example, a dip coating method which pulls up it as it is among a slurry after dipping a base material, One side of the method of applying with a brush, a braid, etc. and a base material is contacted to a slurry, The spin coat method which trickles coating liquid, and the spray coating method which sprays coating liquid on a base material and coats it can be considered rotating the method of decompressing from another side, the method of applying a pressure and pushing in a slurry from one side of a base material, and a base material.

[0071]Although it was made more desirable [for a seed crystal to exist in the fine pores of porous support] in respect of membranous intensity, or resistance to pressure and compactness, it does not interfere in the state where it has adhered to the support surface, either.

[0072]It can be measured with a thin film X-ray diffraction method whether zeolite membrane was made. Specifically CuK α is used for X line source (wavelength = 0.154 nm), an incidence angle is fixed to 3 times, for example, and it is 2 theta about scanning speed. X diffraction measurement can be carried out according to a parallel optical system by a part for 1/4 times. It can identify by comparing the obtained X diffraction pattern with the X diffraction pattern of known literature. By comparing the peak intensity ratio of each peak can consider the stacking tendency of zeolite membrane.

[0073]Although zeolite membrane is coated on porous support as mentioned above, coating of zeolite membrane is good in a 2 times or more line. It is more desirable to carry out twice or more in respect of compactness.

[0074]After generating zeolite membrane, it may add processing of rinsing, desiccation, calcination, etc. It can be checked using the X-ray diffractometer for thin films whether zeolite membrane has formed. When calcinating the generated zeolite membrane, in order not to make the generated zeolite membrane generate a crack, if possible, temperature up is carried out to it, spending them. Below 2 °C / min carry out [below 3 °C / min] temperature up of the heating rate by below 1 °C / min preferably especially still more preferably. Of course, the lower one of a temperature falling speed is good. Below 3 °C / min lower [below 5 °C / min] the temperature falling speed by below 2 °C / min preferably especially still more preferably. Generally calcination temperature is about 150-600 °C.

[0075]When using as the bipolar membrane of inorganic and/or organic polymers the transmission film containing zeolite, after making zeolite by the hydrothermal crystallization method or a steam method beforehand, the particle is mixed with polymers, and a film is produced after that. A method is good if the polymers which it is not restricted to this and zeolite mixed are made. Polymers may be coated after making the film of zeolite. Although the kind in particular of polymer to mix is not limited, they are silicone rubber, polysulfone system polymer, phenol resin, etc.

[0076]As few directions of the transmission film containing zeolite as possible are [holes other than the hole in the crystal of zeolite] good. It is called eburnation processing to

lessen holes other than such inside of a crystal. It is more desirable to perform this eburnation processing to a transmission film, since as few directions of the hole (crevice between crystals) besides such a crystal as possible are good. Even if it does not perform eburnation processing, of course, when the precise film is made, it is not necessary to perform eburnation processing. Although a publicly known method can be used as the method of eburnation processing, Although it does not go into the hole of zeolite as an example, it impregnates with the organic matter of the size which can go into the other hole, for example, the hole produced in the grain boundary between crystals, It calcinates and carbonizes in the gas by which real oxygen, such as nitrogen gas, does not exist after that, and although methods, such as burying those fine pores, are mentioned, it is not limited to this method. Afterbaking is carried out [which was processed with phenol resin etc. which are easy to carbonize], and the hole besides a crystal can be buried or it can also be made bipolar membrane with carbon. You may also embed at the hole which produced high molecular compounds, such as silicone, in the grain boundary, and it may be made bipolar membrane with these. A monomer may be introduced into a grain boundary and it may be made to polymers-ize there.

[0077]Although zeolite may have an ionic exchange point, there is no restriction in particular in the cation currently exchanged for the ionic exchange point. For example, all cations, such as H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Ag^+ , Cu^{2+} , Cu^+ , nickel²⁺, and La^{3+} , are exchangeable, Anything may be contained in the ionic exchange point.

[0078]The stratum functionale in this invention may be an aggregate of only the particles of an inorganic oxide. This is the transmission film which used the micropore of the gap of particles positively unlike zeolite. As the size of particles becomes small, the pole diameter of a transmission film becomes small and is more preferred for penetration selectivity. In this invention, it is preferred that the stratum functionale formed with the inorganic oxide has micropore (2 nm or less). Although the formation method in particular of the stratum functionale by inorganic oxide particles is not limited, spreading, the method of carrying out a dipping, and the method to which oxide particles are made to adhere with chemical vapor deposition at porous support are mentioned to porous support in the colloid which inorganic oxide particles distributed, a slurry, etc. It is the same as explanation concerning the stratum functionale of the above-mentioned zeolite about porous support, eburnation processing, and hydrophobing processing. Composite-ization with other stratum functionale, such as zeolite, a silicone compound, an organic high polymer, and carbon, is also performed preferably.

[0079]Silicone rubber, silicone resin, and/or silicone oil can also be used as a material of the stratum functionale of this invention transmission film. What contains silicone rubber especially is fond, and is used. The silicone told to this invention makes a siloxane bond a skeleton, and puts the organic Si-polymer compound which the organic group etc.

combined with the silicon atom. It is one of the raw materials which consist of silicone, and silicone rubber carries out pons credit of the high-polymer linear polyorganosiloxane to a degree in the middle, it is what showed rubber-like elasticity, and is also called an alias silicone elastomer. Compared with organic system resin, silicone rubber is excellent also in heat resistance and chemical resistance, and can be used also for a not less than 150 ** hot use. Although silicone rubber is classified according to various methods from the character, it can be classified into a hot cure type, a low-temperature vulcanization mold, and a room-temperature-curing type from a point of vulcanizing temperature.

[0080] Hot cure type silicone rubber is silicone of the type with which it is necessary to heat more than the decomposition temperature of a peroxide vulcanizing agent at the time of vulcanization, and rubber elasticity will not be obtained without this. The raw material of hot cure type silicone rubber is mainly a solid state, and although called millable rubber (rubber which can be kneaded), it is not necessarily a solid state.

[0081] On the other hand, cold cure type silicone rubber is liquefied, or the pot life in the ordinary temperature after carrying out paste state and adding a hardening agent is long, and it is excellent in workability. It is a type which hardening follows quickly by not needing the elevated temperature like hot cure type silicone rubber at the time of hardening, but heating at 100 to 150 °C.

[0082] On the other hand, room-temperature-curing type silicone rubber is silicone rubber which a hardening reaction advances at a room temperature and serves as a rubber elastomer literally. Before also hardening room-temperature-curing type silicone rubber, a liquid or paste state is carried out. The difference among these curing temperature changes with the kinds and quantity of the degree of polymerization of the polyorganosiloxane in a raw material, an additive agent, a bulking agent, and a cross linking agent. Although the kind in particular of silicone rubber used for this invention is not limited, from the goodness of workability, low-temperature vulcanization mold silicone rubber and room-temperature-curing type silicone rubber are found, and are used.

[0083] The silicone resin (silicone resin) generally said is also contained in silicone rubber. Compared with the three above-mentioned kinds of silicone rubber, silicone resin is boiled markedly, and its crosslinking density is high, and it is a hard material. Silicone resin is divided roughly into straight silicone resin and silicone modification organosilicon resin. As for straight silicone resin, the ingredient consists only of silicone, and silicone modification organosilicon resin is a copolymer of a silicone component and organic resin. Silicone resin may be used according to required transmission quantity.

[0084] The hardening mechanism of silicone rubber is divided roughly and divided into a condensation reaction type and an addition reaction type. In a condensation reaction type, with the humidity in the air, a condensation reaction occurs and hardening progresses. On the other hand, an addition reaction type is mainly a hydrosilylation reaction (hydrosilylation) reaction, and does not generate a by-product.

[0085] When such a silicone compound is film-ized, compared with porous membrane, such as the above-mentioned zeolite membrane of what penetrates hydrogen etc. well compared with other poly membranes, and an oxide-particles film, the transmission rate of hydrogen is low. As for the reason, silicone membrane and the organic polymer film mentioned later are penetrating the molecule by dissolution diffusion into polymers, and the resistance under penetration of a molecule is considered to be a large thing compared with porous membrane. Therefore, in order to obtain desired transmission quantity, the thinner one of stratum functionale is preferred. However, since selectivity may become low conversely when too not much thin, cautions are required. Although membranous thickness in particular is not limited, 0.1-500 micrometers is preferred. Although desirable thickness varies with a use, in an electrolytic condenser use, about 0.1-200 micrometers is good. It is 0.5-150 micrometers preferably, and is 1-100 micrometers especially preferably. If it becomes such a thin film, only by it, it does not have practical intensity. So, porous support is coated with these stratum functionale in this invention. The gestalt and the directions for a base material are as above-mentioned.

[0086]Although the ingredient in particular of the raw material solution of silicone rubber is not limited, the following ingredients can also be used, for example. First, any silicone rubber uses polyorganosiloxane (silicone polymer) as the main raw material, and the method of adding the increase-in-quantity bulking agents in reinforcing fillers, such as dry process silica and wet process silica, diatomaceous earth, the end of quartz powder, etc., various additive agents, and a cross linking agent to an organic solvent is found, and is applied. The above-mentioned raw material will not be limited especially if it is the dissolution or a thing which can be high-distributed, but the mixed liquor of toluene, xylene, n-heptane, ligroin, isopropyl alcohol, and these organic solvents is found, and the organic solvent used here is used. Although the molecular structure in particular of polyorganosiloxane is not limited, what the methyl group, the phenyl group, the vinyl group, or the trifluoropropyl group combined likes it in silicon, and it is used for it. moreover -- although it is not that to which especially the degree of polymerization of raw material polymer is also limited -- that [10000 or less / the simplicity of coating work to] -- although -- it is used by preference.

[0087]Although the coating method in particular to the base material of silicone rubber is not limited, the following methods can also be used, for example. The method of drawing in from the field of an opposite hand with the field which applies this on a base material after the above-mentioned silicone rubber raw material solution preparation, or dips a base material in the above-mentioned silicone rubber raw material solution, or the above-mentioned silicone rubber raw material solution is contacted to one field of a base material, and carries out the coat of the silicone rubber is applied. After supporting a silicone rubber solution on a base material using ones of these methods, it may process in order to stiffen silicone rubber. As an example of a disposal method, among the atmosphere, it is neglected for 10 minutes - one week, or heats at 200 °C or less, and the method of neglecting it for 10 minutes - one week is found, and is used at a room temperature.

[0088]The carbon which carbonized an organic high polymer or it is also effective as stratum functionale. As an organic high polymer, polyimide, Teflon, petit RENGOMU, isobutylene rubber, Or polypropylene and phenol resin are used preferably and what calcinated polyimide, polyphenol, etc. in a vacuum, a nitrogen air current, inactive gas, or the atmosphere as carbon, and was carbonized is used preferably. The film of an organic high polymer is non-porous membrane as well as the silicone membrane mentioned above, and since the permeability of hydrogen is inferior compared with porous membrane, the thinner one of membranous thickness is preferred. 10micro or less is preferably preferred 100micro or less. As a method of coating porous support with an organic high polymer, polymers are melted in melting or a solvent and they are not spreading, a dipping, and a thing limited to this although the method of spraying is used. After carbon coats beforehand the organic high polymer and organic matter which are easy to carbonize, it can be calcinated and obtained in a vacuum, a nitrogen air current, inactive gas, or the atmosphere. Especially the porous carbon molecular sieve that has fine pores of molecular size also in carbon is preferred. As what carbonizes and becomes a carbon molecular sieve, although polyimide, phenol resin, etc. are mentioned as an example, it is not restricted to this. Although the stratum functionale of an organic high polymer or carbon may be used independently, using by other stratum functionale and composite is also performed preferably.

[0089]This invention relates to the fuel cell system which carries the transmission film or zeolite membrane of the above-mentioned statement.

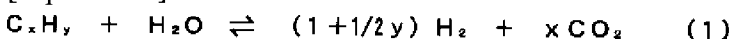
[0090]The fuel cell system expected as a next-generation power generation system is classified into solid polymer type, phosphoric acid type, solid oxide type, and melting carbonate type four according to the ion-exchange membrane to be used. The solid polymer type in this and a phosphoric acid type supply hydrogen to the fuel of a fuel cell, and use a proton conductive film for an ion-exchange membrane. Feeding methods of hydrogen include the method of carrying out direct supply of the hydrogen, and the method of obtaining from hydrocarbon by reforming. If hydrogen gas is efficiently emitted in a reforming reaction, it will not be limited in particular, but aliphatic hydrocarbon and alcohols are found and the hydrocarbon to be used is used. Hydrocarbon that H_2 / CO_2 ratio to generate become high in consideration of an environmental problem is preferred, and methanol and methane are preferred especially. The point that the infrastructure for supplying fuel is fixed to gasoline is also one of the desirable hydrocarbon.

[0091]The reforming method with which a reforming method is usually learned is applied. For example, steam reforming which supplies a steam, and oxidation refining which supplies oxygen and air are used preferably. It is necessary to heat or radiate heat, respectively from steam reforming being an endoergic reaction and oxidation refining being an exoergic reaction. Then, the autothermal method which supplies a steam, oxygen or a steam, and air by a predetermined ratio is also liked and used so that it is not necessary to heat and radiate heat.

[0092]When a steam is used for refining of hydrocarbon, the following reactions occur with a reformer.

[0093]

[Equation 3]



[0094]A small amount of carbon monoxide mixes in reformed gas by the water gas shift reaction shown below.

[0095]

[Equation 4]



[0096]Thus, the carbon monoxide generated by the water gas shift reaction other than hydrogen and carbon dioxide, and the steam and hydrocarbon of a raw material mix in reformed gas.

[0097]In order to fully perform especially a reforming reaction, when a steam is added superfluously, the steam concentration in reformed gas becomes high. If reformed gas with high steam concentration is used, the problem of the activity of a carbon monoxide oxidation catalyst deteriorating, or a steam covering the fuel electrode top of a fuel cell, and reducing generation efficiency will arise. Since hydrogen concentration will fall so much if steam concentration is high, generation efficiency falls. On the other hand, since hydrogen can be selectively penetrated from a steam out of reformed gas if the film of this invention is used, the activity deterioration of a carbon monoxide oxidation catalyst can be controlled, and the fall of hydrogen concentration is controlled, and covering of

the water on a fuel electrode can be suppressed.

[0098]It is known that carbon monoxide generated by a reforming reaction of hydrocarbon will carry out poisoning of the catalyst on a fuel electrode. Therefore, if a film which penetrates hydrogen selectively from carbon monoxide is used, since hydrogen gas with low carbon monoxide concentration can be supplied to a fuel electrode, without using a carbon monoxide oxidation catalyst, it is desirable. In order that there may be no necessity of installing a carbon monoxide oxidation catalyst, it is desirable also from a point which can simplify a device. In order to penetrate hydrogen selectively from carbon monoxide, zeolite membrane which carried out the surface treatment, for example is effective. Silanizing is performed, and using zeolite membrane which made a pole diameter small, a method of separating using a molecular diameter difference of hydrogen and carbon monoxide is found, and is used. If it is not a film which penetrates hydrogen selectively from water also in this case, water which lives together in reformed gas will adsorb in membranous fine pores, and transmission quantity of hydrogen will decrease. Therefore, a film which penetrates hydrogen selectively is very more important also in separation of the hydrogen/carbon monoxide gas under existence of a steam than in water.

[0099]This invention relates to a steam-reforming device which carries a transmission film or zeolite membrane of the above-mentioned statement.

[0100]When carrying out steam reforming of the hydrocarbon, gas which mixed a steam with hydrocarbon is supplied to a 300 to 800 °C reforming catalyst. If a reaction shown in a formula (1) advances to some extent and hydrogen concentration in gas becomes high, contact probability of hydrocarbon and water will fall and reforming reaction speed will fall remarkably. Carbon monoxide which is not preferred generates by (2) types. Then, as shown in drawing 1, in order that a reaction may progress efficiently, reforming reaction speed can be raised by producing some or all of walls of a catalytic reaction tower by this invention film, and removing generated hydrogen gas from water or methanol out of a tower selectively, without a balance ruling over. As a result, it not only can manufacture hydrogen efficiently, but it leads to reduction of carbon monoxide concentration.

Compared with reformed gas generated by the usual reforming reaction, gas which penetrated a film has high hydrogen concentration, and its steam concentration is low. If this gas is supplied to a fuel electrode portion of a fuel cell, an electrode will not be covered with a steam and high electric power will be obtained.

[0101]This invention relates to an electrolytic condenser which carries a transmission film or zeolite membrane of the above-mentioned statement.

[0102]An electrolytic condenser told to this invention is explained in full detail.

[0103]If a transmission film of this invention is used for an electrolytic condenser with which it comes to build in a container an anode terminal and a cathode terminal which anode foil and cathode foil, and an end which were piled up have projected to the exterior of this container, and an electrolysis solution, Since a presentation of an electrolysis solution moreover does not change a lot, either, without internal pressure rising since the transmission film makes hydrogen gas emitted inside a capacitor penetrate and does not make an electrolysis solution penetrate as liquid or a steam, it is dramatically effective in the sense of a life and a stable performance.

[0104]An electrolytic condenser of this invention has the especially outstanding effect, when an electrolysis solution is a liquefied capacitor, although there is no restriction in

particular. In particular, in a large-sized screw-thread terminal type aluminium electrolytic condenser, it is especially effective also in an aluminium electrolytic condenser.

[0105]Hereafter, an electrolytic condenser of this invention is explained based on a drawing. Drawing 2 is an outline cross-sectional view showing an example of an electrolytic condenser which used a transmission film of this invention, and drawing 3 is the outline top view which looked at an obturation plug portion of an electrolytic condenser in drawing 2 from a top.

[0106]That is, in drawing 2, an electrolytic capacitor element which kraft was made to intervene between anode foil and cathode foil, and was wound is impregnated in an electrolysis solution, an anode terminal and a cathode terminal are made to project from a breakthrough of an obturation plug, and it stores in a container made from aluminum. Drawing 3 is a figure showing signs that an obturation plug of drawing 2 was seen from a top, and a transmission film of this invention can be installed with adhesives etc. in a position shown in drawing 3, for example.

[0107]Although a transmission film of this invention penetrates hydrogen, Since hydrogen produced by electrolysis can be missed outside, without changing a presentation of an electrolysis solution that it is hard to penetrate water and ethylene glycol which are the main ingredients of a steam or an electrolysis solution, and gamma-butyrolactone since it is hard to penetrate water, A burst of a capacitor is avoided and performance can be stabilized for a long period of time.

[0108]As for a gestalt of a transmission film used for this invention, a plate-like transmission film is used preferably. Shape in particular of a transmission film does not have restriction, and although a size should be just smaller than a size of an obturation plug, it is preferred that it is smaller than a radius of an obturation plug. A mechanical strength of a grade which restriction does not have thickness in particular of a transmission film, and does not break at the time of setting should just be maintained.

[0109]A film of this invention is not limited to the above-mentioned use.

[0110]For example, after reforming hydrocarbon with a steam, the method at large which makes a film of the above-mentioned statement contact and makes hydrogen penetrate from reformed gas more nearly selectively than a steam is contained in this invention.

[0111]A separation method at large [using a film of the above-mentioned statement] is included in this invention.

[0112]For example, there are many uses which penetrate gas or are separated under existence of polar molecules, such as water, ammonia, and ethylene glycol, and a film provided with character which cannot penetrate easily not only the capability to penetrate gas but the above polar molecules can be used for various uses. For example, it can use for deaeration etc. of dissolved gas in polar solvents, such as separation of nitrogen from air containing a steam, and oxygen, refining of hydrogen from hydrogen gas containing a steam, and water, widely.

[0113]The following examples explain this invention still in detail. But the following example must not be shown for illustration and must not be restrictively interpreted in any meanings.

[0114]

[Example](Example 1) [Composition of the seed crystal for the Silicalite film composition]

In the 20 to 25% solution (Tokyo Chemicals 20 to 25% solution) of 20 g of tetrapropylammonium hydroxide (TPAOH), 0.28 g of sodium hydroxide (the 1st class of reagent by the Katayama chemicals company) was added and stirred. To it, further, 5 g of fumed silica (Aldrich) was added, it heated at 80 **, and transparent solution was obtained. When this was put into the autoclave of a poly ethylene tetrafluoride line and it heated at 125 ** for 8 hours, the particles (mean particle diameter of about 80 nm) of Silicalite were obtained. Water was added to this and it was considered as Silicalite colloid of 1wt% Silicalite content.

[0115](Example 2) [Coating to the porous support of a seed crystal]

1wt% of the Silicalite colloid 0.1g obtained in Example 1, the square whose one side is 1.4 cm -- the porous support (what was coated only with thing:one side which cut the ceramics membrane by NGK Insulators, Ltd. (100mmX100mmX3mm) in this size by about 50 micrometers in thickness in the alumina particle.) of 3-mm-thick alpha-alumina After dropping the average pore size as uniformly as possible and coating it on the field processed by a 0.1-micrometer alumina particle, it dried, and it was calcinated at 550 ** for 3 hours, and obtained the base material with which the coat of the seed crystal was carried out.

[0116](Example 3) [Manufacture and evaluation of ZSM-5 film by a steam method]

To the field where the Silicalite particles (stratum-functionale precursor) of the porous support by which the coat was carried out were coated, the seed crystal obtained in Example 2. 40 SiO₂ : 0.8aluminum₂O₃ : 12 TPAOH (tetrapropylammonium hydroxide) : 0.1g was dropped, it was made to dry at a room temperature overnight, and gel of the presentation of 430H₂O was used as the sample film. Ludox HS-40 (product made from Du Pont) was used for the source of SiO₂, and Pural (product made from CONDEA) was used for the source of aluminum₂O₃. Like drawing 6, 0.5 g of water was put in 50-ml autoclave, the above-mentioned sample film was put on the stand made from poly ethylene tetrafluoride, it was installed in autoclave, and it heated for five days at 150 ** by steam continence pressing down (this operation is hereafter called steam treatment). It rinsed and checked that the thin film of ZSM-5 formed on porous support after desiccation with the X diffraction and the electron microscope. Next, this film-like sample was calcinated at 550 ** for 2 hours. The heating rate at the time of calcination was made into 0.6**/min., and the temperature falling speed was made into 1.2**/min. It checked that the thin film of ZSM-5 (silica / alumina ratio 50) formed after calcination on porous support as a result of an X diffraction and electron microscope observation.

[0117](Example 4) [Creation of the cell for transit measurement]

This device is explained using drawing 4. This device is a product made from stainless steel, and supplies gas from a gas supplying port. The transmission film is being fixed via silicone rubber which is an elastic body.

The field which has the stratum fonctionale of a transmission film has turned to the gas side shown in a gas supplying port.

In order to prevent gas leaking from the crevice between silicone rubber and a transmission film, in the field which has the stratum fonctionale of a transmission film, the field of the opposite hand is suppressed by the metal fittings made from stainless steel. Since it is being fixed with the O ring, the gas after penetrating a transmission film leaks from other than a penetration gas outlet, and does not come out of these metal fittings.

[0118](Example 5) [Measurement of the hydrogen permeation speed using the cell for transit measurement]

The transmission rate of hydrogen gas of the film produced in Example 3 was measured using the device shown in Example 4. When the amount of hydrogen gas which installed the penetration device under 20 ** atmosphere, supplied 2-atmosphere hydrogen to the gas supply side of a device, and penetrated the film was measured with the soap film flow meter, it was 15.0×10^{-7} (mol/(m² and s-Pa)). Next, the penetration device was installed in oven and it heated at 65 ** in oven. When 2-atmosphere hydrogen was supplied to the gas supply side of a device, the hydrogen gas which penetrated the film was sent to the soap film flow meter which is under 20 ** atmosphere through the pipe made from stainless steel and the flow was measured, it was 13.8×10^{-7} (mol/(m² and s-Pa)). Next, heat at 85 ** in oven and 2-atmosphere hydrogen is supplied to the gas supply side of a device, When the hydrogen gas which penetrated the film was sent to the soap film flow meter which is under 20 ** atmosphere through the pipe made from stainless steel and the flow was measured, it was 13.6×10^{-7} (mol/(m² and s-Pa)).

[0119]Next, again, temperature up of the film produced and calcinated in Example 3 was carried out by 0.6 (a part for **/) from a room temperature to 550 **, it was held at 550 ** for 4 hours, and was lowered by 1.2 (a part for **/) from 550 ** to the room temperature. When hydrogen permeation speed was measured with the described method at the room temperature, it was 15.5×10^{-7} (mol/(m² and s-Pa)). The transmission rate after 2 times calcination became large about 3.3% from the transmission rate after 1-time calcination.

[0120](Example 6) [Hydrogen / water vapor transmission rate ratio]

Water was taken in the test tube and the weight was measured. The zeolite membrane shown in the penetration device shown in Example 4 in Example 3 apart from this was fixed. The gas supplying port of a penetration device and the mouth of the test tube were connected with the rubber tube. This whole device was kept warm at 65 **, and saturated steam in 65 ** was put to the film. This device was picked out from oven every several hours, it cooled radiationally at the room temperature, and the weight of a test tube and water was measured. The average loss-in-quantity speed of water was drawn from weight loss in quantity of cooking time and water. As a result, it was 4.8×10^{-3} g/h-cm². this water vapor transmission rate is 0.38×10^{-7} (mol/(m² and s-Pa)) -- a ratio with hydrogen permeation speed of 65 ** -- V_{H_2}/V_{H_2O} was 36.

[0121](Example 7) [Hydrogen / ethylene glycol transmission rate ratio]

Ethylene glycol was taken in the test tube and the weight was measured. The zeolite membrane shown in the penetration device shown in Example 4 in Example 3 apart from this was fixed. The gas supplying port of a penetration device and the mouth of the test tube were connected with the rubber tube. This whole device was kept warm at 85 **, and the saturated ethylene glycol steam in 65 ** was put to the film. This device was picked out from oven every several hours, it cooled radiationally at the room temperature, and the weight of a test tube and ethylene glycol was measured. The average loss-in-quantity speed of ethylene glycol was drawn from weight loss in quantity of cooking time and ethylene glycol. As a result, it was 4.9×10^{-4} g/h-cm². this ethylene glycol transmission rate is 2.1×10^{-8} (mol/(m² and s-Pa)) -- a ratio with hydrogen permeation speed of 85 ** -- V_{H_2}/V_{EG} was 65.

[0122](Example 8) [Creation of an electrolytic condenser]

1wt% of the Silicalite colloid 0.1g obtained in Example 1 9 mm in diameter. the porosity cylindrical base material (what was coated only with thing:one side which processed the NGK Insulators, Ltd. film production by about 50 micrometers in thickness in the alumina particle.) of 2-mm-thick alpha-alumina After dropping the average pore size as uniformly as possible and coating it on the field processed by a 0.1-micrometer alumina particle, it dried, and it was calcinated at 550 ** for 3 hours, and obtained the pellet with which the coat of the seed crystal was carried out. It is this Ludox HS-30 After having been immersed in 1 g, Pural 0.01g, the 20%TPAOH solution 1g, and the mixed liquor of the water 2.48g, pulling up and neglecting it at ordinary temperature for 1 hour, it heated for five days at 150 ** under steam application of pressure. This film-like sample was calcinated at 550 ** after rinsing for 2 hours. The heating rate at the time of calcination was made into 0.6**/min., and the temperature falling speed was made into 1.2**/min. The thin film of Silicalite checked forming on a base material with the X diffraction and the electron microscope.

[0123]As shown in drawing 5, the spring was applied to the non treating surface of the pellet, and this was put in the upper part and the lower part of the obturation plug, and it fixed. A large-sized screw-thread terminal type electrolytic condenser like drawing 2 was made using this obturation plug.

[0124](Example 9) [Production of a steam-reforming device]

an alumina tube (construction material: -- alpha-alumina, inside diameter:7mm, and outer diameter: -- 10 mm) Length: After applying 0.12 g/cm² of 1wt% Silicalite seed crystal solutions which produced alpha-alumina particle with a particle diameter of 0.1 micrometer in Example 1 to the wall of 50-micrometer thickness coating on 300 mm and a wall, it calcinated at 500 **. One mouth of the alumina pipe was closed, and from the mouth of the open one, zeolite precursor sol (Ludox HS-30 1g, Pural0.01g, the 20%TPAOH solution 1g, and mixed liquor of the water 2.48g) was poured in, and it settled for 2 minutes. Then, after throwing away the liquid in a pipe and drying an alumina pipe at a room temperature, it heated for five days at 150 ** under steam application of pressure. This cylinder film-like sample was calcinated at 550 ** after rinsing for 2 hours. The heating rate at the time of calcination was made into 0.6**/min., and the temperature falling speed was made into 1.2**/min. The thin film of ZSM-5 checked forming on the wall of a pipe with the X diffraction and the electron microscope. These 16 tubular films were made into the shape of a bundle tied like drawing 6, and the zeolite membrane module was produced. This was filled up with the copper-zinc system methanol reforming catalyst as shown in drawing 1, and the steam-reforming device was produced.

[0125](Example 10) [Production of a fuel cell system]

A fuel cell system is explained based on drawing 7. The pipeline who can mix the gas which penetrated the transmission film which constitutes the wall of this steam-reforming device, and the gas discharged from the exit of a device was connected using the steam-reforming device shown in Example 9. The air feeder was connected to this pipeline. This pipeline was connected to the carbon monoxide selective oxidation catalyst device. The pipeline was connected so that the gas discharged from this catalyst device could be supplied to the fuel electrode part of a fuel cell, and the fuel cell system was produced.

[0126](Comparative example 1) [Manufacture and evaluation of the Silicalite film by a steam method]

To the field where the Silicalite particles (stratum-functionale precursor) of the porous support by which the coat was carried out were coated, the seed crystal obtained in Example 2. 40 SiO₂ : 12 TPAOH (tetrapropylammonium hydroxide) : 0.1g was dropped, it was made to dry at a room temperature overnight, and gel of the presentation of 430H₂O was used as the sample film. Ludox HS-40 (product made from DuPont) was used for SiO₂ source. Steam treatment of this was carried out. It rinsed and checked that the thin film of Silicalite formed on porous support after desiccation with the X diffraction and the electron microscope. Next, this film-like sample was calcinated at 550 °C for 2 hours. The heating rate at the time of calcination was made into 0.6°C/min., and the temperature falling speed was made into 1.2°C/min. It checked that the thin film of Silicalite formed after calcination on porous support as a result of an X diffraction and electron microscope observation.

[0127]The penetration characteristic was evaluated in accordance with the method of Examples 5, 6, and 7. As for 3.2×10^{-7} (mol/(m² and s-Pa)) and hydrogen selectivity, 6.3 and V_{H2}/V_{EG} of V_{H2}/V_{H2O} were [transmission rate of hydrogen] 12.8.

[0128]

[Effect of the Invention]This invention relates to the film which penetrates hydrogen selectively from a steam or ethylene glycol. This transmission film is used suitably for the separation or the penetration of gas under the conditions in which the polar high compound steam of water, ethylene glycol, gamma-butyrolactone, ammonia, etc. exists. This film can be used also as the film for various gas permeation under the situation where a polar high compound steam does not exist, of course, or a film for a liquid penetration.

[0129]This invention relates to application and the pertinent art of this transparent membrane again. The transmission film of this invention can be used for the use of a fuel cell, an electrolytic condenser, etc., for example. Although a fuel cell uses hydrogen as fuel, this hydrogen is obtained by receiving supply of direct hydrogen or reforming hydrocarbon, such as methanol, methane, and gasoline, with a steam etc. The method of reforming hydrocarbon is advantageous at the point which can carry out the weight saving of the fuel stores dept., and the point in which an infrastructure building is comparatively easy. Water, carbon monoxide, and carbon dioxide are contained in the gas generated when steam reforming of the stretcher hydrogen was carried out in addition to hydrogen. When the steam concentration in reformed gas is high, there is a fault of falling the activity of a carbon monoxide reforming catalyst and hydrogen concentration falling, and covering a fuel electrode and reducing generation efficiency. On the other hand, since hydrogen can be selectively penetrated from reformed gas if the film of this invention is used during a steam reforming reaction or after refining, the efficiency of a reforming reaction can be increased and hydrogen can be taken out efficiently.

[0130]If the transmission film of this invention is used for an electrolytic condenser, the life of the conventionally publicly known electrolytic condenser which had caused breakage with the pressure of the hydrogen gas emitted inside the hermetic container can fully be extended, and the safety of an electrolytic condenser in use can also secure it.

TECHNICAL FIELD

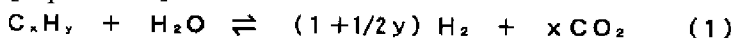
[Field of the Invention] This invention relates to the film which penetrates hydrogen selectively from a steam or ethylene glycol. This transmission film is used suitably for the separation or the penetration of gas under the conditions in which the polar high compound steam of water, ethylene glycol, gamma-butyrolactone, ammonia, etc. exists. This transmission film can be used also as the film for various gas permeation under the situation where a polar high compound steam does not exist, of course, or a film for a liquid penetration.

[0002] This invention relates to application and the pertinent art of this transmission film again. The transmission film of this invention can be used for the use of a fuel cell, an electrolytic condenser, etc., for example.

[0003] Although a fuel cell uses hydrogen as fuel, this hydrogen is obtained by receiving supply of direct hydrogen or reforming hydrocarbon, such as methanol, methane, and gasoline, with a steam etc. The system which supplies hydrogen directly is advantageous at the point which can simplify the structure of a system. However, when a high-pressure-hydrogen cylinder and a liquid hydrogen tank are used, it is a problem in respect of safety or weight, and when a hydrogen storing metal alloy is used, the point of a price and weight poses a problem. It is a problem also at the point that the infrastructure for supplying hydrogen is not fixed. On the other hand, although a reformer etc. are needed and the structure of a system is complicated, the method of reforming hydrocarbon has a lightweight fuel stores dept., and it is thought that maintenance of the infrastructure which supplies fuel is easier for it than hydrogen. When a steam is used for refining of hydrocarbon, the following reactions occur with a reformer.

[0004]

[Equation 1]

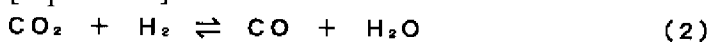


[0005] Since this reaction is static reaction, if hydrogen and carbon dioxide are selectively removable from a reformer, it can advance a reaction more. Therefore, the film which penetrates selectively hydrogen which is a resultant from the water which is reaction raw materials is very important.

[0006] A small amount of carbon monoxide mixes in reformed gas by the water gas shift reaction shown below.

[0007]

[Equation 2]



[0008] It is known that carbon monoxide will carry out poisoning of the catalyst on a fuel electrode. Therefore, generation of CO can be suppressed if H₂ and CO₂ are quickly removable from a reforming reaction system. The film which penetrates hydrogen selectively can also remove the carbon monoxide which is a poisoning substance of a fuel electrode, and is still more useful than carbon monoxide. If it is not a film which penetrates hydrogen selectively from water also in this case, the water which lives together in reformed gas will adsorb in membranous fine pores, and the transmission

quantity of hydrogen will decrease. Therefore, the film which penetrates hydrogen selectively is very more important also in separation of the hydrogen/carbon monoxide gas under existence of a steam than in water.

[0009]The transmission film of this invention can also be used for an electrolytic condenser. The electrolysis solution is held in a hermetic container, an electrolysis solution decomposes gradually during an electrolytic condenser operation, and hydrogen gas generates an electrolytic condenser. The electrolytic condenser had caused breakage with the pressure of the emitted hydrogen gas. If the transmission film of this invention is used, the life of an electrolytic condenser can fully be extended and the safety of an electrolytic condenser in use can also secure it.

[Translation done.]

CLAIMS

[Claim(s)]

[Claim 1]Hydrogen permeation speed in $65^{**} V_{H_2}$ (mol/(m² and s-Pa)) and a water vapor transmission rate A ratio of V_{H_2O} (mol/(m² and s-Pa)) V_{H_2}/V_{H_2O} 20 or more. And hydrogen permeation speed in 85^{**} A ratio of V_{H_2} (mol/(m² and s-Pa)) and ethylene glycol steamy transmission rate V_{EG} (mol/(m² and s-Pa)) That V_{H_2}/V_{EG} is 50 or more. A transmission film which does not use as the main ingredients palladium by which it is characterized.

[Claim 2]A transmission film which fills the following (1) and the characteristic of (2).

(1) Hydrogen permeation speed in 25^{**} should be more than 10×10^{-7} (mol/(m² and s-Pa)).

(2) When you stop a test tube containing ethylene glycol by this film, you put into 85^{**} oven and you measure the loss-in-quantity speed, the value should be below 6×10^{-3} (g/hour) per 1 cm of film².

[Claim 3]The transmission film according to claim 1 or 2, wherein hydrogen permeation speed after performing once heat-treatment in the air of (1) to (3) shown below in order of (1) to (3), and hydrogen permeation speed after carrying out twice in order of (1) to (3) do not change not less than 10%.

(1) It is 0.6 (a part for $^{**}/$) from a room temperature to 550^{**} , and is temperature up.

(2) Hold at 550^{**} for 4 hours.

(3) Lower the temperature by 1.2 (a part for $^{**}/$) from 550^{**} to a room temperature.

[Claim 4]A transmission film of claims 1-3 containing at least one ingredient of the following ingredient of (1) to (5) given in any 1 paragraph.

(1) Zeolite (2) inorganic-oxide particle (3) silicone rubber, silicone resin, or silicone oil

(4) organic polymer compound (5) carbon [Claim 5]The transmission film according to

claim 4, wherein SiO_2 /aluminum₂O₃ of zeolite are 30 or more.

[Claim 6]The transmission film according to claim 5, wherein zeolite is MFI type zeolite.

[Claim 7]A manufacturing method of zeolite membrane using boehmite or quasi-boehmite as an alumina source.

[Claim 8]A manufacturing method of the zeolite membrane according to claim 7 processing with a steam a filmy material which has a silica source and an alumina source.

[Claim 9]A fuel cell system which carries zeolite membrane obtained by transmission film of claim 1-6 given in any 1 paragraph, claim 7, or a manufacturing method given in 8.

[Claim 10]A steam-reforming device of hydrocarbon which carries zeolite membrane obtained by transmission film of claim 1-6 given in any 1 paragraph, claim 7, or a manufacturing method given in 8.

[Claim 11]An aluminium electrolytic condenser which carries zeolite membrane obtained by transmission film of claim 1-6 given in any 1 paragraph, claim 7, or a manufacturing method given in 8.

[Claim 12]How to contact reformed gas to zeolite membrane obtained by transmission film of claim 1-6 given in any 1 paragraph, claim 7, or a manufacturing method given in 8, and to make hydrogen penetrate from reformed gas more nearly selectively than a steam after reforming hydrocarbon with a steam.

[Claim 13]A separation method of a gas or a fluid using zeolite membrane obtained by transmission film of claim 1-6 given in any 1 paragraph, claim 7, or a manufacturing method given in 8.

PRIOR ART

[Description of the Prior Art]Conventionally, palladium membrane is known as a film which makes hydrogen penetrate selectively. For example, in steam reforming of methane, it is also possible to lean a reaction equilibrium to the output side remarkably by making the hydrogen to generate penetrate selectively. However, the hydrogen permeation mechanism of palladium membrane is a dissolution diffusion mechanism accompanied by dissociation of hydrogen.

In order for a utilization level to gather a transmission rate, hydrogen gas must be supplied by not less than 300 ** and tens of atmospheres.

The application for the fuel cell and electrolytic condenser use of this penetration condition from severity is difficult. Palladium is dramatically expensive and it is difficult to use in practice industrially also from this point.

[0011]As a method of removing carbon monoxide from the gas (example: gas which carried out steam reforming of the hydrocarbon) containing the hydrogen supplied to a fuel cell, the method of oxidizing only carbon monoxide selectively on a catalyst is proposed. In JP,11-130406,A, the method of making oxygen react to reformed gas on the catalyst which supported platinum group system metal to zeolite, and removing carbon monoxide is proposed. In JP,10-247154,A, the method of using the catalyst which supported rhodium and a ruthenium to zeolite, silica, or alumina is proposed. However, in these methods, since a selective oxidation catalyst tower and its heating unit are carried, a device is large and is complicated. When a steam superfluous at the time of refining is used, into reformed gas, a steam mixes, catalytic activity is reduced, and a superfluous steam cannot be removed.

[0012]On the electrolytic condenser field and in JP,62-112314,A or JP,62-272515,A, Although the method of discharging the hydrogen gas emitted in an electrolytic

condenser outside using the transmission film of the shape of a hollow filament which consists of polyimide, poly ethylene tetrafluoride, or polypropylene, etc. are proposed, an effect until it still discharges hydrogen gas enough and carries out internal pressure rise prevention is not enough. In an electrolytic condenser, since an electrolysis solution penetrated as a steam from an electrolytic condenser, there was a big fault that the presentation of internal electrolysis liquid changed and the characteristic of an electrolytic condenser changed.

[0013]Although the film using zeolite is studied briskly in recent years, it is difficult to obtain zeolite membrane with the specific penetration characteristic with sufficient reproducibility. Although hydrogen permeation speed in 25 ** penetrates well the film which are $10 \times 10^{-7} \text{ mol / (m}^2\text{/s/Pa)}$ above, and (1) (2) hydrogen, a steam and/or ethylene glycol are not proposed until now about the zeolite membrane which is hard to penetrate.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]This invention relates to the film which penetrates hydrogen selectively from a steam or ethylene glycol. This transmission film is used suitably for the separation or the penetration of gas under the conditions in which the polar high compound steam of water, ethylene glycol, gamma-butyrolactone, ammonia, etc. exists. This film can be used also as the film for various gas permeation under the situation where a polar high compound steam does not exist, of course, or a film for a liquid penetration.

[0129]This invention relates to application and the pertinent art of this transparent membrane again. The transmission film of this invention can be used for the use of a fuel cell, an electrolytic condenser, etc., for example. Although a fuel cell uses hydrogen as fuel, this hydrogen is obtained by receiving supply of direct hydrogen or reforming hydrocarbon, such as methanol, methane, and gasoline, with a steam etc. The method of reforming hydrocarbon is advantageous at the point which can carry out the weight saving of the fuel stores dept., and the point in which an infrastructure building is comparatively easy. Water, carbon monoxide, and carbon dioxide are contained in the gas generated when steam reforming of the stretcher hydrogen was carried out in addition to hydrogen. When the steam concentration in reformed gas is high, there is a fault of falling the activity of a carbon monoxide reforming catalyst and hydrogen concentration falling, and covering a fuel electrode and reducing generation efficiency. On the other hand, since hydrogen can be selectively penetrated from reformed gas if the film of this invention is used during a steam reforming reaction or after refining, the efficiency of a reforming reaction can be increased and hydrogen can be taken out efficiently.

[0130]If the transmission film of this invention is used for an electrolytic condenser, the life of the conventionally publicly known electrolytic condenser which had caused breakage with the pressure of the hydrogen gas emitted inside the hermetic container can fully be extended, and the safety of an electrolytic condenser in use can also secure it.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]The purpose of this invention is what is going to cancel the fault of the above-mentioned conventional technology, It is in providing the film which cannot penetrate easily (2) ethylene-glycol steam which is excellent in heat resistance and chemical resistance, penetrates hydrogen well excluding expensive metal substantially like hydrogen and affinitive palladium, and cannot penetrate a steam as easily as (1) hydrogen.

[0015]Other purposes of this invention are related with application and the pertinent art of this transmission film, and there are in providing the fuel cell system which has the above-mentioned transmission film which utilizes the permeability of the above-mentioned transmission film effectively, the steam-reforming device of hydrocarbon, and an aluminium electrolytic condenser.

[Translation done.]

MEANS

[Means for Solving the Problem]To achieve the above objects, as a result of inquiring wholeheartedly, it resulted in an invention which has the following composition.

[0017]The invention of this invention according to claim 1 is hydrogen permeation speed in 65 **, V_{H_2} (mol/(m² and s-Pa)) and water vapor transmission rate Ratio of V_{H_2O} (mol/(m² and s-Pa)) V_{H_2}/V_{H_2O} 20 or more. And hydrogen permeation speed in 85 ** V_{H_2} (mol/(m² and s-Pa)) and ethylene glycol steamy transmission rate Ratio with V_{EG} (mol/(m² and s-Pa)) That V_{H_2}/V_{EG} is 50 or more. It is a transmission film which does not use as the main ingredients palladium by which it is characterized.

[0018]The invention of this invention according to claim 2 is a transmission film which fills the following (1) and the characteristic of (2).

[0019](1) Hydrogen permeation speed in 25 ** should be more than 10×10^{-7} (mol/(m² and s-Pa)).

[0020](2) When you stop a test tube containing ethylene glycol by this film, you put into 85 ** oven and you measure the loss-in-quantity speed, the value should be below 6×10^{-3} (g/hour) per 1 cm of film².

[0021]A process of zeolite membrane which processes with a steam a filmy material which has that boehmite or quasi-boehmite is used for this invention as an alumina source and/or a silica source, and an alumina source is included.

[0022]An electrolytic condenser which has a transmission film or zeolite membrane of a

steam-reforming device and the above-mentioned statement which has a transmission film or zeolite membrane of a fuel cell system and the above-mentioned statement in which this invention has a transmission film or zeolite membrane of the above-mentioned statement is contained.

[0023]A method of making a transmission film or zeolite membrane of the above-mentioned statement of reformed gas contact, and making hydrogen penetrate from reformed gas more nearly selectively than a steam, after this invention reforms hydrocarbon with a steam is contained.

[0024]The invention of this invention according to claim 14 is an invention about a separation method of a gas which used a transmission film or zeolite membrane of a statement for the above, or a fluid.

[0025]

[Embodiment of the Invention]This invention is explained in full detail below.

[0026]First, the transmission film of this invention is explained.

[0027]The transmission film of this invention is hydrogen permeation speed in 65 **. V_{H_2} (mol/(m² and s-Pa)) and water vapor transmission rate Ratio of V_{H_2O} (mol/(m² and s-Pa)) V_{H_2}/V_{H_2O} 20 or more. And hydrogen permeation speed in 85 ** V_{H_2} (mol/(m² and s-Pa)) and ethylene glycol steamy transmission rate Ratio with V_{EG} (mol/(m² and s-Pa)) That V_{H_2}/V_{EG} is 50 or more. It is a transmission film which does not use as the main ingredients the palladium by which it is characterized. As a film which hydrogen penetrates selectively, although precise films, such as palladium membrane, are known, what penetrates hydrogen with selectivity higher than a steam and ethylene glycol by the film which does not use palladium as the main ingredients is not known until now.

[0028]This invention relates to the transmission film which fills the following (1) and the characteristic of (2).

[0029](1) The hydrogen permeation speed in 25 ** should be more than 10×10^{-7} (mol/(m² and s-Pa)).

[0030](2) When you stop the test tube containing ethylene glycol by this film, you put into 85 ** oven and you measure the loss-in-quantity speed, the value should be below 6×10^{-3} (g/hour) per 1 cm of film².

[0031]While a room temperature shows a big hydrogen permeation speed in this way, the film which cannot penetrate ethylene glycol easily is not known until now.

[0032]Although the whole transmission film of the transmission film said here may be made of construction material which has hydrogen permeation selectivity, in order that it may usually enlarge a transmission rate, The method of supporting the film which penetrates hydrogen selectively is liked and used from a steam and/or ethylene glycol on the porous support which has macro pore. Thus, the film which penetrates hydrogen selectively from the steam and/or ethylene glycol which were supported on macro pore porous support is called stratum functionale (or functional membrane). In order to show the permeability of the invention film indicated to claim 2, the thinner one of the thickness of the stratum functionale is preferred. Although the desirable thickness of the stratum functionale changes with raw materials of the stratum functionale to choose, 500 micrometers or less are 100 micrometers or less desirable still more preferably. If the stratum functionale is thin, the thinner one is preferred, but it becomes not much thin too much, and compactness must not be lost. It is saying that there being compactness does not have a hole resulting from the pinhole or defect instead of a meaning of being

nonporous.

[0033]It is used in order to prevent the portion of the stratum functionale weak [intensity] or weak from the porous support used by this invention breaking thinly, and the upright thing of porous support is preferred.

[0034]It may be unable to simplify and, in the case of porous support which becomes, the stratum functionale may be unable to be protected from destruction. In the film of intensity which the porous support itself touches by hand simply, and breaks, it is not suitable for industrial practical use.

[0035]Since this invention relates to a transmission film, as a base material which supports the stratum functionale, the porosity of the grade which does not check the permeability of the stratum functionale is required for it.

[0036]If the construction material of porous support has the above character, it will not be limited in particular, but ceramics, such as metal and a metallic oxide, and organic polymer are mentioned as an example. From a viewpoint of intensity or stiffness, ceramics, such as metal and a metallic oxide, are used preferably. From a viewpoint heat-resistant and chemical-resistant, a metallic oxide is used most preferably especially. Especially as a metallic oxide, although not limited, alumina, zirconia, silica, mullite, cordierite, a titania, zeolite, or a zeolite prototype is used preferably. As a metaled example, the porous support made from stainless steel (sintered metal), etc. are mentioned. In the use for which heat resistance is not required, if the porous support of organic polymer is also upright, it can use. In order to prevent destruction of a stratum-functionale portion also in this case, when it is going to bend by hand, what has the stiffness of the grade at which it does not see and turn by the eye is preferred.

[0037]The thing of shape usually marketed, such as a globular shape, plate-like, tube shape, the shape of a monolith, and honeycomb shape, can be used, for example, without also limiting especially the shape of porous support. When using for an electrolytic condenser, porous support is the shape where a cylindrical plate is the most preferred. When using it as a demarcation membrane, high surface area is required for porous support, and it is preferred that it is the shape of a tube, a monolith, or honeycomb shape.

[0038]The manufacturing method of porous support used by this invention, Although not limited in particular, usually the auxiliary agent and binder for molding can be added to powder, such as remaining as it is or ceramics, and extrusion molding of the powder, such as ceramics, can be carried out to it, or press forming can be performed, and the method of manufacturing can be adopted through processes, such as desiccation and calcination.

[0039]Although the optimal calcination temperature changes with raw materials of porous support, its temperature which is a grade from which sintering begins for a while is desirable in respect of intensity. Although suitable calcination temperature changes with sizes of a raw material or particles, generally it is 900-1,400 ** especially preferably 800-1,500 ** preferably 600 ** - 2,000 **. Washing by a drug solution etc., etc. may be processed after calcination. Coating with fine particles, controlling the pole diameter of porous support by methods, such as dip coating, controlling compatibility with the stratum functionale by them, or controlling surface roughness by them is also preferably performed to the fabricated porous support. Although the layer by such coating etc. is called interlayer, providing one or more layers of this interlayer is preferably performed, also when using which stratum functionale.

[0040]When the pore diameter of porous support is too large, the stratum functionale does not film-size, but a hole produces, or, Or it is got blocked, and since the distance in which stratum-functionale raw material liquid permeates too much into the fine pores of porous support, and the hole of porous support is eventually closed by the stratum functionale and in which gas penetrates the inside of the stratum functionale becomes long too much, the fault that sufficient amount of gas permeation is not obtained may arise. Therefore, 10 micrometers or less are preferred and 5 micrometers or less of average pore sizes [1 micrometer or less of] of porous support are less than 0.5 micrometer especially preferably still more preferably still more preferably. Thus, the above-mentioned interlayer is preferably used also in the meaning which controls a pore diameter. Although the minimums of an average pore size differ and cannot be specified with the molecular size made to penetrate, it is better for there to be an average pore size of 0.01 micrometers or more from a penetrable viewpoint of a request molecule.

[0041]The average pore size of porous support can usually be measured using the mercury porosimeter. If the size of the ceramics particles which constitute the interlayer is uniform in simple, even if the size of the particle is called average pore size, there will be no great difference.

[0042]The stratum functionale may be formed in any portion of porous support in the transmission film of this invention. The stratum functionale can be formed in both one side of porous support, both the surfaces, or the surfaces and insides. When forming the stratum functionale, in the point of control of the thickness of the stratum functionale, it is preferred to coat on the surface of porous support, and it is preferred to form in the inside of porous support in respect of the intensity of the stratum functionale. In tube shape porous support, even if it coats the inside, it does not matter even if it coats outside. Also in the porous support of the shape of a monolith, or honeycomb shape, although the stratum functionale may be provided anywhere, since surface area can do greatly the direction coated inside in these cases, it is desirable.

[0043]The measuring method of the hydrogen permeation speed said by this invention is described below. For example, 2-atmosphere hydrogen gas is supplied to one side of the transmission film of 1 cm², and the gas volume penetrated from a membranous opposite hand is measured with a soap film flow meter. If this method is used, a transmission rate when 1 cc/s of hydrogen gas penetrates will serve as 4.5×10^{-6} (mol/(m² and s-Pa)).

EXAMPLE

[Example](Example 1) [Composition of the seed crystal for the Silicalite film composition]

In the 20 to 25% solution (Tokyo Chemicals 20 to 25% solution) of 20 g of tetrapropylammonium hydroxide (TPAOH), 0.28 g of sodium hydroxide (the 1st class of reagent by the Katayama chemicals company) was added and stirred. To it, further, 5 g of fumed silica (Aldrich) was added, it heated at 80 **, and transparent solution was obtained. When this was put into the autoclave of a poly ethylene tetrafluoride line and it heated at 125 ** for 8 hours, the particles (mean particle diameter of about 80 nm) of Silicalite were obtained. Water was added to this and it was considered as Silicalite

colloid of 1wt% Silicalite content.

[0115](Example 2) [Coating to the porous support of a seed crystal]

1wt% of the Silicalite colloid 0.1g obtained in Example 1, the square whose one side is 1.4 cm -- the porous support (what was coated only with thing:one side which cut the ceramics membrane by NGK Insulators, Ltd. (100mmX100mmX3mm) in this size by about 50 micrometers in thickness in the alumina particle.) of 3-mm-thick alpha-alumina After dropping the average pore size as uniformly as possible and coating it on the field processed by a 0.1-micrometer alumina particle, it dried, and it was calcinated at 550 ** for 3 hours, and obtained the base material with which the coat of the seed crystal was carried out.

[0116](Example 3) [Manufacture and evaluation of ZSM-5 film by a steam method]

To the field where the Silicalite particles (stratum-functionale precursor) of the porous support by which the coat was carried out were coated, the seed crystal obtained in Example 2. 40 SiO₂ : 0.8aluminum₂O₃ : 12 TPAOH (tetrapropylammonium hydroxide) : 0.1g was dropped, it was made to dry at a room temperature overnight, and gel of the presentation of 430H₂O was used as the sample film. Ludox HS-40 (product made from Du Pont) was used for the source of SiO₂, and Pural (product made from CONDEA) was used for the source of aluminum₂O₃. Like drawing 6, 0.5 g of water was put in 50-ml autoclave, the above-mentioned sample film was put on the stand made from poly ethylene tetrafluoride, it was installed in autoclave, and it heated for five days at 150 ** by steam continence pressing down (this operation is hereafter called steam treatment). It rinsed and checked that the thin film of ZSM-5 formed on porous support after desiccation with the X diffraction and the electron microscope. Next, this film-like sample was calcinated at 550 ** for 2 hours. The heating rate at the time of calcination was made into 0.6**/min., and the temperature falling speed was made into 1.2**/min. It checked that the thin film of ZSM-5 (silica / alumina ratio 50) formed after calcination on porous support as a result of an X diffraction and electron microscope observation.

[0117](Example 4) [Creation of the cell for transit measurement]

This device is explained using drawing 4. This device is a product made from stainless steel, and supplies gas from a gas supplying port. The transmission film is being fixed via silicone rubber which is an elastic body.

The field which has the stratum fonctionale of a transmission film has turned to the gas side shown in a gas supplying port.

In order to prevent gas leaking from the crevice between silicone rubber and a transmission film, in the field which has the stratum fonctionale of a transmission film, the field of the opposite hand is suppressed by the metal fittings made from stainless steel. Since it is being fixed with the O ring, the gas after penetrating a transmission film leaks from other than a penetration gas outlet, and does not come out of these metal fittings.

[0118](Example 5) [Measurement of the hydrogen permeation speed using the cell for transit measurement]

The transmission rate of hydrogen gas of the film produced in Example 3 was measured using the device shown in Example 4. When the amount of hydrogen gas which installed the penetration device under 20 ** atmosphere, supplied 2-atmosphere hydrogen to the gas supply side of a device, and penetrated the film was measured with the soap film flow meter, it was 15.0×10^{-7} (mol/(m² and s-Pa)). Next, the penetration device was installed in

oven and it heated at 65 °C in oven. When 2-atmosphere hydrogen was supplied to the gas supply side of a device, the hydrogen gas which penetrated the film was sent to the soap film flow meter which is under 20 mm atmosphere through the pipe made from stainless steel and the flow was measured, it was 13.8×10^{-7} (mol/(m² and s-Pa)). Next, heat at 85 °C in oven and 2-atmosphere hydrogen is supplied to the gas supply side of a device, When the hydrogen gas which penetrated the film was sent to the soap film flow meter which is under 20 mm atmosphere through the pipe made from stainless steel and the flow was measured, it was 13.6×10^{-7} (mol/(m² and s-Pa)).

[0119]Next, again, temperature up of the film produced and calcinated in Example 3 was carried out by 0.6 (a part for °C) from a room temperature to 550 °C, it was held at 550 °C for 4 hours, and was lowered by 1.2 (a part for °C) from 550 °C to the room temperature. When hydrogen permeation speed was measured with the described method at the room temperature, it was 15.5×10^{-7} (mol/(m² and s-Pa)). The transmission rate after 2 times calcination became large about 3.3% from the transmission rate after 1-time calcination.

[0120](Example 6) [Hydrogen / water vapor transmission rate ratio]

Water was taken in the test tube and the weight was measured. The zeolite membrane shown in the penetration device shown in Example 4 in Example 3 apart from this was fixed. The gas supplying port of a penetration device and the mouth of the test tube were connected with the rubber tube. This whole device was kept warm at 65 °C, and saturated steam in 65 °C was put to the film. This device was picked out from oven every several hours, it cooled radiationally at the room temperature, and the weight of a test tube and water was measured. The average loss-in-quantity speed of water was drawn from weight loss in quantity of cooking time and water. As a result, it was 4.8×10^{-3} g/h-cm². this water vapor transmission rate is 0.38×10^{-7} (mol/(m² and s-Pa)) -- a ratio with hydrogen permeation speed of 65 °C -- V_{H_2}/V_{H_2O} was 36.

[0121](Example 7) [Hydrogen / ethylene glycol transmission rate ratio]

Ethylene glycol was taken in the test tube and the weight was measured. The zeolite membrane shown in the penetration device shown in Example 4 in Example 3 apart from this was fixed. The gas supplying port of a penetration device and the mouth of the test tube were connected with the rubber tube. This whole device was kept warm at 85 °C, and the saturated ethylene glycol steam in 65 °C was put to the film. This device was picked out from oven every several hours, it cooled radiationally at the room temperature, and the weight of a test tube and ethylene glycol was measured. The average loss-in-quantity speed of ethylene glycol was drawn from weight loss in quantity of cooking time and ethylene glycol. As a result, it was 4.9×10^{-4} g/h-cm². this ethylene glycol transmission rate is 2.1×10^{-8} (mol/(m² and s-Pa)) -- a ratio with hydrogen permeation speed of 85 °C -- V_{H_2}/V_{EG} was 65.

[0122](Example 8) [Creation of an electrolytic condenser]

1wt% of the Silicalite colloid 0.1g obtained in Example 1 9 mm in diameter. the porosity cylindrical base material (what was coated only with thing:one side which processed the NGK Insulators, Ltd. film production by about 50 micrometers in thickness in the alumina particle.) of 2-mm-thick alpha-alumina After dropping the average pore size as uniformly as possible and coating it on the field processed by a 0.1-micrometer alumina particle, it dried, and it was calcinated at 550 °C for 3 hours, and obtained the pellet with which the coat of the seed crystal was carried out. It is this Ludox HS-30 After having

been immersed in 1 g, Pural 0.01g, the 20%TPAOH solution 1g, and the mixed liquor of the water 2.48g, pulling up and neglecting it at ordinary temperature for 1 hour, it heated for five days at 150 °C under steam application of pressure. This film-like sample was calcinated at 550 °C after rinsing for 2 hours. The heating rate at the time of calcination was made into 0.6°C/min., and the temperature falling speed was made into 1.2°C/min. The thin film of Silicalite checked forming on a base material with the X diffraction and the electron microscope.

[0123]As shown in drawing 5, the spring was applied to the non treating surface of the pellet, and this was put in the upper part and the lower part of the obturation plug, and it fixed. A large-sized screw-thread terminal type electrolytic condenser like drawing 2 was made using this obturation plug.

[0124](Example 9) [Production of a steam-reforming device]

an alumina tube (construction material: -- alpha-alumina, inside diameter:7mm, and outer diameter: -- 10 mm) Length: After applying 0.12 g/cm² of 1wt% Silicalite seed crystal solutions which produced alpha-alumina particle with a particle diameter of 0.1 micrometer in Example 1 to the wall of 50-micrometer thickness coating on 300 mm and a wall, it calcinated at 500 °C. One mouth of the alumina pipe was closed, and from the mouth of the open one, zeolite precursor sol (Ludox HS-30 1g, Pural0.01g, the 20%TPAOH solution 1g, and mixed liquor of the water 2.48g) was poured in, and it settled for 2 minutes. Then, after throwing away the liquid in a pipe and drying an alumina pipe at a room temperature, it heated for five days at 150 °C under steam application of pressure. This cylinder film-like sample was calcinated at 550 °C after rinsing for 2 hours. The heating rate at the time of calcination was made into 0.6°C/min., and the temperature falling speed was made into 1.2°C/min. The thin film of ZSM-5 checked forming on the wall of a pipe with the X diffraction and the electron microscope. These 16 tubular films were made into the shape of a bundle tied like drawing 6, and the zeolite membrane module was produced. This was filled up with the copper-zinc system methanol reforming catalyst as shown in drawing 1, and the steam-reforming device was produced.

[0125](Example 10) [Production of a fuel cell system]

A fuel cell system is explained based on drawing 7. The pipeline who can mix the gas which penetrated the transmission film which constitutes the wall of this steam-reforming device, and the gas discharged from the exit of a device was connected using the steam-reforming device shown in Example 9. The air feeder was connected to this pipeline. This pipeline was connected to the carbon monoxide selective oxidation catalyst device. The pipeline was connected so that the gas discharged from this catalyst device could be supplied to the fuel electrode part of a fuel cell, and the fuel cell system was produced.

[0126](Comparative example 1) [Manufacture and evaluation of the Silicalite film by a steam method]

To the field where the Silicalite particles (stratum-functionale precursor) of the porous support by which the coat was carried out were coated, the seed crystal obtained in Example 2. 40 SiO₂ : 12 TPAOH (tetrapropylammonium hydroxide) : 0.1g was dropped, it was made to dry at a room temperature overnight, and gel of the presentation of 430H₂O was used as the sample film. Ludox HS-40 (product made from DuPont) was used for SiO₂ source. Steam treatment of this was carried out. It rinsed and checked that the thin film of Silicalite formed on porous support after desiccation with the X diffraction and

the electron microscope. Next, this film-like sample was calcinated at 550 °C for 2 hours. The heating rate at the time of calcination was made into 0.6°C/min., and the temperature falling speed was made into 1.2°C/min. It checked that the thin film of Silicalite formed after calcination on porous support as a result of an X diffraction and electron microscope observation.

[0127]The penetration characteristic was evaluated in accordance with the method of Examples 5, 6, and 7. As for 3.2×10^{-7} (mol/(m² and s-Pa)) and hydrogen selectivity, 6.3 and V_{H_2}/V_{EG} of V_{H_2}/V_{H_2O} were [transmission rate of hydrogen] 12.8.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a schematic diagram showing an example of the steam-reforming machine using the transmission film of this invention.

[Drawing 2]It is an outline cross-sectional view showing an example of the electrolytic condenser using the transmission film of this invention.

[Drawing 3]It is the outline top view which looked at the obturation plug portion of the electrolytic condenser in drawing 2 from the top.

[Drawing 4]It is an outline side view for explaining the cell for permeation performance measurement of the transmission film of this invention.

[Drawing 5]It is a figure shown in how to attach the zeolite membrane to the obturation board in drawing 3. (Zeolite membrane is attached to the obturation board via silicone rubber which is an elastic body.)

[Drawing 6]It is a figure showing what modularized the tubular zeolite membrane of this invention in the shape of a bundle.

[Drawing 7]It is a schematic diagram of a fuel cell system using the transmission film of this invention.

[Translation done.]

DRAWINGS

[Drawing 1]

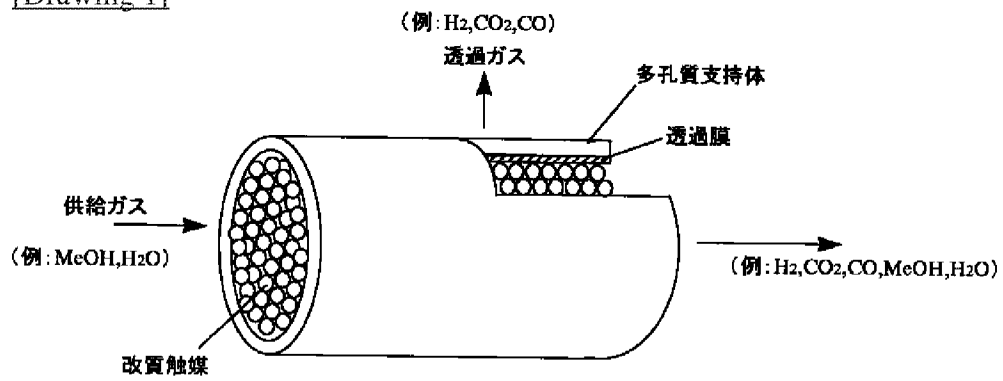


図1 水蒸気改質装置

[Drawing 2]

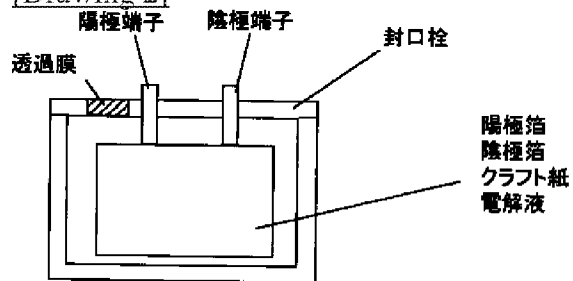


図2 電解コンデンサ断面図

[Drawing 3]

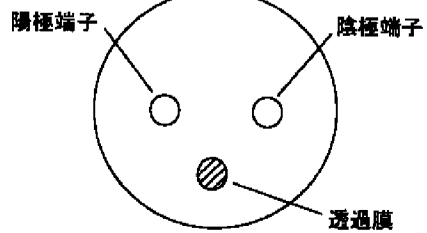


図3 封口栓正面図

[Drawing 4]

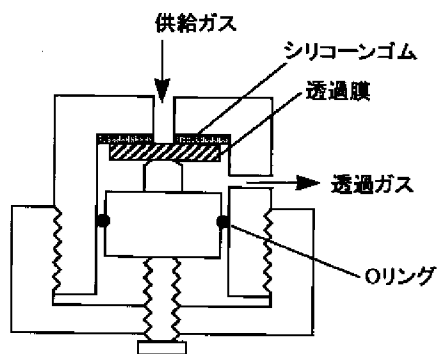


図4 ステンレス製水素透過装置

[Drawing 5]

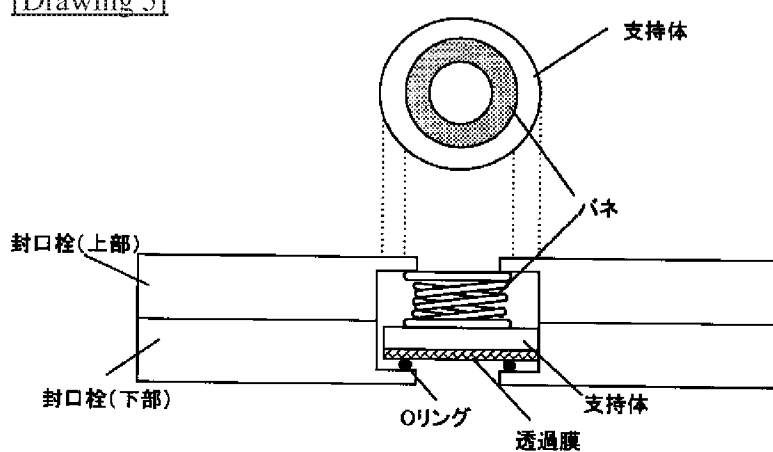


図5 透過膜の封口板への取り付け方

[Drawing 6]

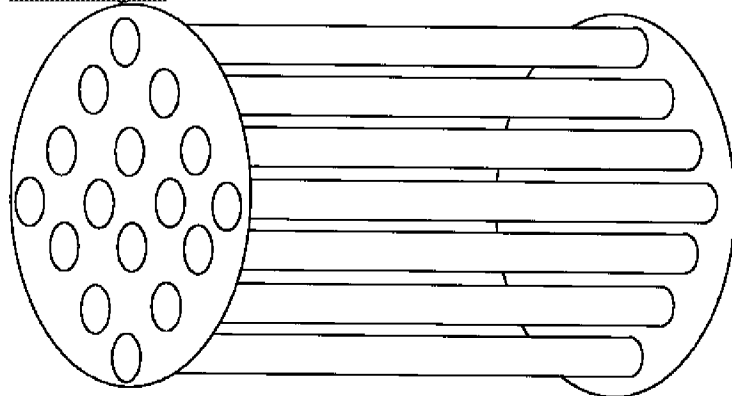


図6 透過膜モジュール

[Drawing 7]

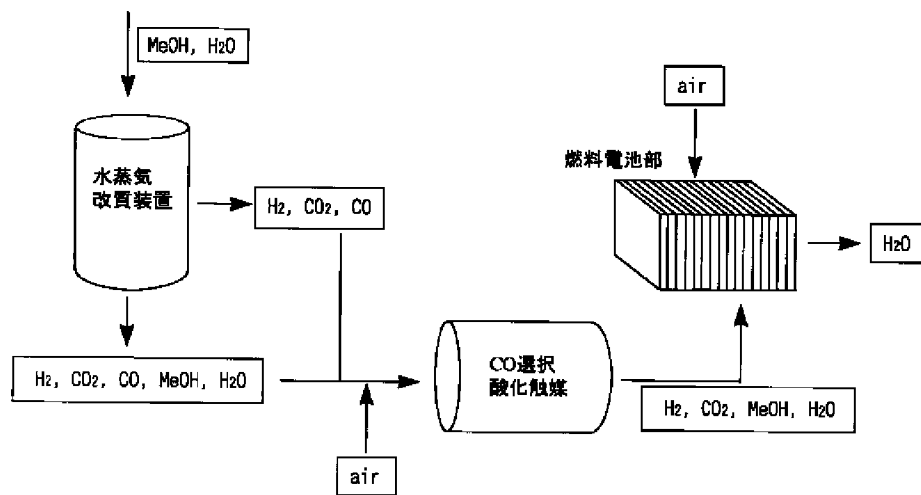


図7 透過膜を組み込んだ燃料電池システム

[Translation done.]